



Identification and Laboratory Assessment of Best Practices to Protect DOT Equipment from the Corrosive Effect of Chemical Deicers



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SI* (MODERN METRIC) CONVERSION FACTORS				
APPROXIMATE CONVERSIONS TO SI UNITS				
Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
AREA				
in ²	square inches	645.2	square millimeters	mm ²
ft ²	square feet	0.093	square meters	m ²
yd ²	square yard	0.836	square meters	m ²
ac	acres	0.405	hectares	ha
mi ²	square miles	2.59	square kilometers	km ²
VOLUME				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft ³	cubic feet	0.028	cubic meters	m ³
yd ³	cubic yards	0.765	cubic meters	m ³
NOTE: volumes greater than 1000 L shall be shown in m ³				
MASS				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
TEMPERATURE (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
ILLUMINATION				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²
FORCE and PRESSURE or STRESS				
lbf	poundforce	4.45	newtons	N
lbf/in ²	poundforce per square inch	6.89	kilopascals	kPa
APPROXIMATE CONVERSIONS FROM SI UNITS				
Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
AREA				
mm ²	square millimeters	0.0016	square inches	in ²
m ²	square meters	10.764	square feet	ft ²
m ²	square meters	1.195	square yards	yd ²
ha	hectares	2.47	acres	ac
km ²	square kilometers	0.386	square miles	mi ²
VOLUME				
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m ³	cubic meters	35.314	cubic feet	ft ³
m ³	cubic meters	1.307	cubic yards	yd ³
MASS				
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
TEMPERATURE (exact degrees)				
°C	Celsius	1.8C+32	Fahrenheit	°F
ILLUMINATION				
lx	lux	0.0929	foot-candles	fc
cd/m ²	candela/m ²	0.2919	foot-Lamberts	fl
FORCE and PRESSURE or STRESS				
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in ²

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2003)

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Abstract

This study has identified, evaluated and synthesized the best practices that can be implemented to minimize the corrosive effects of chloride deicers on DOT winter application equipment and vehicles. The practices identified include: design improvements, maintenance practices, anti-corrosion coatings, corrosion inhibitors, salt removers, etc. A comprehensive literature search was conducted to gather existing research documents that are relevant to the corrosion of metals by chloride salts, with a focus on corrosion under neutral pH conditions and under ambient temperature and pressure. A nationwide survey was conducted of stakeholder groups, in order to capture the current knowledge in: estimating the deicer corrosion costs to vehicles and equipment, defining the chloride deicer corrosion problem and identifying best practices or products for managing the problem.

The survey results suggest that chloride-based deicers are the most commonly used products for highway winter maintenance operations and pose significant corrosion risk to DOT equipment and vehicles. The survey results show that chloride deicers pose the most significant risk of metallic corrosion to dump trucks followed by liquid deicer applicators, front end loaders and hoppers. Most metallic components on vehicles and equipment are very vulnerable to chloride deicer corrosion, and this risk is especially high for electrical wiring, frames, brackets and supports, brake air cans, brake drums and disks, spreader chute, fittings, and granular hopper. Cast irons have seen the most serious general corrosion, followed by carbon steels, composites, and magnesium alloys. Aluminum alloys and stainless steels have seen the most serious localized corrosion, followed by metallic glass, metallic coatings, and magnesium alloys.

The agency survey identified annual expenditures in the current practices of managing deicer-related metallic corrosion in the equipment fleet of responding agencies that report it as being a significant issue. The findings are summarized as follows.

	Training programs	Materials selection	Design improvements	Corrosion monitoring /testing	Proactive maintenance	Reactive maintenance
No. of Responses	8	15	9	1	14	8
Average	\$190,938	\$320,667	\$45,000	\$10,000	\$171,424	\$325,000
Standard Deviation	\$342,845	\$568,651	\$43,157	NA	\$279,106	\$319,598
Coefficient of Variance	180%	177%	96%	NA	163%	98%

The agency survey also identified the current risks and annual costs of deicer corrosion to the equipment fleet of responding agencies that report it as being a significant issue, estimated under the current level of corrosion management. The findings are summarized as follows.

	Depreciation in value	Increased downtime	Reduced reliability	Reduced service life	Increased premature repair and replacement	Safety risk due to faulty parts
No. of Responses	12	13	9	12	7	4
Average	17.3%	8.5%	11.9%	17.3%	19.6%	1.5%
Standard Deviation	12.6%	8.3%	8.7%	12.6%	12.2%	1.0%
Coefficient of Variance	73%	98%	74%	73%	62%	67%

	Depreciation in value	Increased downtime	Reduced reliability	Reduced service life	Increased premature repair and replacement	Safety risk due to faulty parts
No. of Responses	9	6	5	4	5	1
Average	\$12,512,227	\$69,167	\$172,000	\$1,127,750	\$139,224	\$30,000
Standard Deviation	\$27,053,553	\$94,943	\$205,597	\$1,121,133	\$72,729	NA
Coefficient of Variance	216%	137%	120%	99%	52%	NA

Under the investigated conditions, the best-performing coating (*Rust Bullet*), spray-on corrosion inhibitor (*Krown*) and salt removers (*HoldTight* and *ChlorRid*) were identified and they all showed outstanding performance in providing corrosion protection to the carbon steel substrate against $MgCl_2$ solutions. From the wet-dry test, it can be concluded that the power-washing with salt remover *HoldTight* (to a less extent, soapy water) can significantly enhance the anti-corrosion property of carbon steel (1008 CS) and stainless steel (204 SS) in $MgCl_2$ solutions. However, no significant benefits were observed from power-washing with *HoldTight* in protecting the aluminum alloy (1100 Al) against corrosion by $MgCl_2$. The data also imply that once active corrosion of metals started, the benefits of simply power-washing in reducing the corrosion rate of metals would diminish.

Environment exposure studies were performed by the Southwest Research Institute[®] (SwRI[®]) to further investigate the potential benefits of select corrosion inhibitors and anti-corrosion coating in mitigating the deicer corrosion of vehicle component materials. *In situ* corrosion data, including both general and maximum localized corrosion rates, acquired from each multi-electrode array sensor (MAS) are used to assess the corrosion inhibition in an accelerating manner.

- For all three materials in both $MgCl_2$ and NaCl exposure environments, the most severe corrosion occurred at the beginning of humid stage. Therefore, reducing dry-wet exposure cycles will effectively decrease material corrosion, especially localized corrosion. Even though the cyclic exposure to diluted $MgCl_2$ poses more corrosion risk to 314 SS and 1008 CS than that to diluted NaCl, such risks are better mitigated by the spray-on corrosion inhibitors tested.

- Periodically spraying a corrosion inhibitor (*Krown T40*, 19 times per year) would effectively protect the aluminum, stainless steel, and carbon steel components on DOT equipment from corrosion related to NaCl or MgCl₂ deicers, by reducing their corrosion rate by at least 99%. Similarly, a one-time application of protective coating (*Rust Bullet*) reduced their corrosion rate by at least 99.5%, but additional research is needed to improve the integrity and durability of such coating over the years of field exposure.

For the entire WSDOT fleet, the corrosion-related repair costs and preventative maintenance (PM) costs averaged 4.3% and 12.9% of the all repair costs (excluding PM costs), respectively. For the WSDOT snowplows, the corrosion-related repair costs and PM costs averaged 9.3% and 10.1% of the all repair costs (excluding PM costs), respectively. This highlights the fact that snowplows tend to corrode much faster than other WSDOT equipment, likely due to their more extensive exposure to roadway deicers.

For an “average agency” (e.g., a northern state DOT with an average size of fleet asset), one can assume that it is possible to reduce the total cost of corrosion risks related to deicer exposure by 25%, if the agency can increase its investment in equipment corrosion management by 75% and focus more on proactive maintenance (vs. reactive maintenance). As such, the benefit/cost ratio of further improving deicer corrosion management of DOT equipment fleet can be estimated to be 4.4.

For the WSDOT (with an equipment asset of \$168,558,632), one can assume that it is possible to reduce the total cost of corrosion risks related to deicer exposure by 20%, if WSDOT can increase its investment in equipment corrosion management by 75% and focus more on proactive maintenance (vs. reactive maintenance). As such, the benefit/cost ratio of further improving deicer corrosion management of DOT equipment fleet can be estimated to be 8.

Implementation Recommendations

1. Wherever possible, agencies should consider using corrosion-inhibited products or non-chemical means (e.g., pavement technologies) for snow and ice control, so as to reduce the deicer corrosion to DOT equipment, other vehicles, and possibly transportation infrastructure. This recommendation is based solely on the corrosion risk inherent in chloride deicers, and does not consider other dimensions of the deicer usage such as cost, performance, and chlorides or abrasives loading in water bodies.

2. Agencies should consider corrosion-resistance requirements at the stages of materials selection and design. Existing knowledge about the anti-corrosion performance of various materials and design configurations in various deicer-laden service environments should be utilized to refine the equipment purchasing specifications developed by the transportation agencies. For instance, the zinc coating on steel substrates can provide good anti-corrosion performance. Structures designed for resistance to atmospheric corrosion should always provide easy drainage from all exposed surfaces. Stress corrosion cracking (SCC) can be prevented by substituting a more resistant alloy, removing the tensile stress, or making the environment less aggressive. Crevice corrosion can be minimized by proper design of welded

joints and gaskets that minimize crevices. ***Contact between dissimilar metals can lead to galvanic corrosion and should be avoided wherever possible.*** Alternatively, modifications should be made to DOT equipment to mitigate the risk of deicer corrosion. For instance, WSDOT implemented the following best practices: use of high-quality weather-proof terminations (e.g., buss-style connectors and compression fittings) in equipment specifications; elimination of junction boxes wherever possible, relocation of junction boxes to inside the cab off the floor; use of sealed brake canisters and sealed protective boxes surrounding hydraulic components and batteries; and, use of high-quality weather-proof terminations and compression fittings in addition to shrink wrapping susceptible electrical wiring components. Some additional best practices by others: eliminating areas that solids and liquids may accumulate; specifying rust-proof brake shoes when rebuilding; specifying self-healing undercoats for chassis; specifying fender liners for chassis; using dielectric silicone for sealing damaged areas or connections; opening up closed areas (e.g. pillars) and allowing them to flush out easily; using welds to close and seal off certain areas that are difficult to drain; caulking welds prior to painting; avoiding any damage of wiring insulation; etc. Finally, certain corrosion-prone components should use corrosion-resistant materials (e.g., stainless steel or non-metallic) or be inspected and replaced on a regular basis (e.g., replacing truck radiators every two years).

3. Wherever possible, agencies should consider de-humidified storage of their equipment and vehicles. Or at least store equipment in dry climate after washing. This is expected to minimize the risk of metallic corrosion and extend the service life of equipment and vehicles. Relative to NaCl, MgCl₂ and CaCl₂ are more hygroscopic and thus their residue on the bare metals in the equipment can lead to higher risk of corrosion, even in seemingly dry environments (e.g., RH of 35%).

4. Agencies should implement an extensive preventative maintenance program to preserve the value and performance of their equipment and vehicles. For instance, WSDOT implemented the following best practices: consistent washing after application, regular rinsing and localized cleaning (followed by fast drying), using high-quality primers and topcoats in equipment specifications, using composite materials less susceptible to corrosion, and protecting new and replacement components prior to installation with wraps, covers, or shields. Power-wash with salt remover *HoldTight* or similar product to significantly enhance the anti-corrosion property of carbon steel and stainless steel parts against deicer corrosion. Once active corrosion of metals started, power-washing should be coupled with other means, e.g., applying spray-on corrosion inhibitor (e.g., *Krown T40*, 19 times per year) immediately after the equipment is washed clean and dried. Other methods of aftermarket rust-proofing may include the application of post-assembly coatings (e.g., *Rust Bullet*).

5. Agencies should implement reactive maintenance practices to minimize the negative impact of deicer corrosion to their equipment and vehicles. For instance, WSDOT implemented the following best practices: neutralizing the existing corrosion (e.g., via abrasive blasting and steam cleaning and/or chloride neutralizer spray) and cleaning the area or material that was corroded.

6. Agencies should track the data relevant to analyzing the direct costs of deicer corrosion to their equipment asset and the direct benefits of countermeasures, so as to enable reliable, quantitative cost-benefit analysis. Currently, there is a clear absence of documented information, both in the published literature and in the practitioner community that spells out such quantified values. Regardless of the issues that may be inherent to specific items, agencies should consider revising the corrosion management information they currently collect if a more rigorous understanding of the costs and benefits associated with deicer corrosion to equipment is desired.

7. Additional research is recommended to bridge some existing knowledge gaps relevant to this subject. First of all, research is needed to optimize the use of best practices or products for corrosion protection of vehicles and equipment and to evaluate their long-term effectiveness. For instance, there is currently a lack of information on the cost-effectiveness of automated internal washing mechanisms and other effective washing techniques, relative to a low-volume high-pressure washing system. It is desirable to test the field performance of regular washing (with salt remover) and innovative anti-corrosion products. Secondly, additional research should be conducted to explore methods to minimize the risk of premature failure of the post-assembly coatings (e.g., *Rust Bullet*), both on boldly exposed surfaces and within occluded sites. Thirdly, research is needed to assess the effectiveness and benefits in the synergistic use of frequent washing, salt remover, corrosion inhibitor, and possibly coating to protect the DOT equipment. Fourthly, research is needed to identify, develop, and evaluate technologies to on-line assess the condition of key metallic components and their applied coatings so that maintenance of the metal or coating can be performed based on the corrosion condition. Finally, research is needed to develop best practice guidelines (e.g., a user's corrosion management guide) once laboratory and field studies are conducted to validate the best practices against deicer corrosion.

CHAPTER 1 - INTRODUCTION

1.1. Problem Statement

Deicer corrosion to winter application equipment and vehicles was ranked as number 3 out of 20 research needs identified by the winter maintenance practitioners of State Departments of Transportation (DOTs) at the 2nd National Winter Maintenance Peer Exchange (2009). This highlights the urgent need of conducting a comprehensive evaluation of best practices in managing such risk related to the use of snow and ice control chemicals.

Today's motor vehicles and winter maintenance application vehicles have a wide array of metals in them, e.g., steel (for frames, bumpers, brake lines, body panels, fuel tanks, fittings, exhaust systems, etc.), cast irons (for engines and drive train components, brake drums and disks, fittings, etc.), aluminum alloys (for body panels, fuel tanks, trim, radiators, wheels, engine and drive train components, fittings, etc.), magnesium alloys (for wheels, transmission housings, brackets and supports, etc.), and copper and copper alloys (for electrical wiring, radiators, brake line fittings, etc.). All of these metallic components are subject to the corrosive effects of snow and ice control materials (a.k.a., deicers).

The corrosion of motor vehicles due to road salts was estimated to cost \$2.8 billion to \$5.6 billion per year, including the added manufacturing expense for vehicle protection and preventive maintenance and the cost of owner preventive maintenance and cosmetic-corrosion-related vehicle depreciation [1]. A more recent study estimated the total cost of corrosion to motor vehicles (from road salts as well as other culprits e.g., marine environment) to be \$23.4 billion per year [2]. A 1985-1990 field study in Sweden revealed that compared with those exposed to (NaCl) salted roads, the cars driven on unsalted roads had 50% less incidence of cosmetic corrosion and the carbon steel test panels had a more than 90% reduction in corrosion rate [3]. There are a variety of thermodynamic and kinetic factors (e.g., humidity, chloride concentration, dissolved oxygen, pH, temperature) that determine the tendency and rate of vehicle corrosion respectively, which can take the form of general corrosion or localized corrosion (galvanic corrosion, pitting corrosion, filiform corrosion, poultice corrosion, crevice corrosion, intergranular corrosion, erosion corrosion, stress corrosion cracking - SCC, corrosion fatigue, microbially influenced corrosion, etc.). Note that since the 1970s the industry has adapted to the NaCl based deicers via better vehicle design and materials selection; however, the increased use of magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$) based deicers poses a new threat to be addressed. Different from NaCl, the $MgCl_2$ and $CaCl_2$ based deicers feature a hygroscopic nature and can continue to draw moisture from air even in seemingly dry environments. The same mechanism enables these chemicals to work as effective dust suppressants.

According to a recent U.S. National Cooperative Highway Research Program (NCHRP) report [4], "crevice corrosion and poultice corrosion typically occur where dirt and moisture are trapped – between adjacent pieces of metal, under gaskets and at fasteners, or on the surface of motor vehicle components. This is compounded by ingress of snow and ice control chemicals and other ionic materials (e.g., acid rain) that increase the conductivity of the trapped moisture. Aluminum alloys are more prone to crevice corrosion and galvanic corrosion when coupled to steel". In a case study conducted by the Western Transportation Institute (WTI), we investigated the corrosion of trucks exposed to deicers applied on

Montana highways and observed significant crevice corrosion between the conjunction of winch frame and truck frame and in conjunctions on truck frame as well as filiform corrosion under the coating near frame corners and on brake chambers. We also observed other forms of less significant corrosion on the trucks, such as pitting corrosion on the outer surfaces of stainless steel parts and aluminum fuel tanks, galvanic corrosion and SCC in the welding zones or conjunction of dissimilar metals [5].

In a two-year field study of the deicer corrosion to specimens mounted on winter maintenance equipment [6], the researchers observed intergranular corrosion attack on all 5182-O Al specimens (as shown in Figure 1) and a few A356 cast Al specimens and general corrosion on all 1008 steel and most A356 cast Al specimens. A 0-12% decrease in tensile strength was observed among Al specimens evaluated (and other specimens in the first year), depending on severity of corrosion. The researchers concluded that materials loading, exposure miles, climatic conditions (humidity, temperature, etc.), washing frequencies, and other factors (e.g., abrasives and debris) all influenced the corrosion rates of vehicle-mounted specimens. Similarly, a laboratory study [35] revealed that AISI 4140 steel would show a lower fatigue strength once corroded via exposure to 3.5 wt.% sodium chloride (NaCl) or calcium magnesium acetate (CMA) solutions.

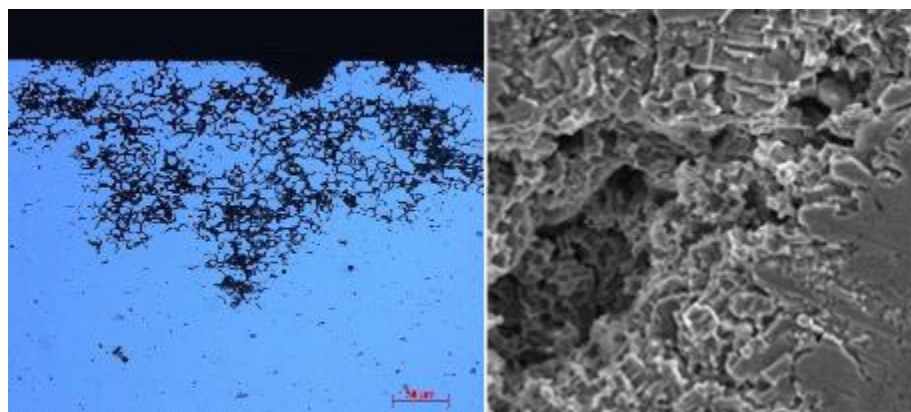


Figure 1. SEM evidence of selective attack of grain boundary (left) and Mg_2Al_3 precipitates (right) on Al specimens exposed to field chloride-based deicers [6]

There are many technologies available to mitigate the corrosion of metals, by either enhancing the inherent corrosion resistance and performance of the metal itself, or reducing the corrosivity of the service environment, or altering the metal/electrolyte interface (e.g., salt extracting agents/rust-converters, corrosion inhibitors, metallic coatings, non-metallic coatings, and surface treatment of metals). These countermeasures can be used individually or synergistically in the practices of managing the corrosive effects of deicers to motor vehicles and winter maintenance application equipment. A 1970-1972 field study at the Kennedy Space Center (Florida) Corrosion Test Site investigated the effectiveness of various corrosion protection methods for Ground Support Equipment (GSE) Applications [36]. The two-year field exposure study revealed that: 1) for aluminum alloys, a three-coat paint system and inorganic zinc paint provided complete protection (against the chloride-laden environment); 2) for stainless steels, sacrificial type coatings (e.g., zinc-rich and aluminum-rich paints), polyethylene tape, and a fluidized-bed epoxy provided excellent protection; 3)

for galvanized steel parts, none of the treatments evaluated significantly extended the life of the zinc coating; 4) for carbon steels, a vapor-phase corrosion-inhibiting compound protected the internal surfaces of enclosures subject to moisture intrusion while none of the treatments applied to external surfaces gave adequate long-term protection. Palmer (1992) suggested that regular wash operations (coupled with the addition of environmentally acceptable corrosion inhibitors) and aftermarket rust-proofing (coating formulations able to displace moisture and penetrate corrosion product layers) can both be effective solutions in mitigating deicer corrosion to motor vehicles [37]. Payer (1992) suggested that a combination of environmental stresses can lead to the failure of automotive electronics, often initiated at the contact surfaces of connectors. As such, resistance to corrosive (chemical), thermal, and mechanical stresses are essential for connector reliability and the corrosion protection of the connector and contact surfaces can be achieved via proper design, materials selection and the use of seals/grommets and lubricants [38].

In this context, there is an urgent need to identify best practices that can be used to preserve the quality and life of DOT equipment and vehicles at risk of deicer corrosion. In May 2011, a two-year study was initiated at WTI to address this need. Note that this study (especially the laboratory investigation) focused on the metallic corrosion aggravated by sodium chloride and magnesium chloride based deicers. Calcium chloride based deicers may lead to similar metallic corrosion to a different extent, but they are beyond the scope of this study.

1.2. Study Objective

The objective of this project is to identify, evaluate and synthesize best practices that can be implemented to minimize the effects of deicer corrosion on DOT winter application equipment and vehicles. To this end, this study consists of a comprehensive literature review, agency survey, site visit, laboratory investigation, and cost-benefit analysis, as detailed later.

CHAPTER 2 – METHODOLOGY

2.1. Literature Review

The literature search and synthesis were conducted to document the state of the practice and the state of the art related to this project, with a focus on: the corrosive effect of chloride and non-chloride deicers to metals, the assessment of deicer corrosion to metals (e.g., test protocols), the identification of corrosion-prone parts on equipment/vehicles and their common forms of corrosion and related failure, and the mitigation of such corrosion via design improvements, maintenance practices, or the use of coatings and corrosion inhibitors, etc. A literature synthesis consisting of six chapters is given as **Appendix A** and the key findings are also presented in Chapter 3.

Research conducted in European countries, China and by other international sources were reviewed wherever available, along with the ongoing research and existing documents published by the National Association of Corrosion Engineers (NACE), DOTs, University Transportation Centers (UTCs), Transportation Research Board (TRB), etc. The research team conducted keyword searches of several databases to gather relevant information including:

- Google Scholar (<http://www.scholar.google.com>)
- NACE database
- SCIFinder Scholar (<http://www.cas.org/SCIFINDER/SCHOLAR/>)
- SCIRus (<http://www.scirus.com>)
- CorrDefense (<http://www.corrdefense.org>)
- Patent Office (<http://patft.uspto.gov/netahtml/PTO/search-adv.htm>) or Google Patents
- DOD STINET (<http://stinet.dtic.mil/>)
- STN Database (<http://info.cas.org/ONLINE/DBSS/itrdss.html>)
- Montana State University Library (<http://www.lib.montana.edu/>)

2.2. Survey of Transportation Professionals

The purpose of the survey was to gain insight on the current practice related to best practices or products used by various industries and agencies to protect their equipment or vehicles from the corrosive effects of chloride deicers. The survey consisted of 15 multipart questions and was published online at <https://www.surveymonkey.com/s/ZL77RPB>. The survey was distributed to various professional forums, including NACE Corrosion Network, Corrosion Prevention Association (CPA), equipment engineers, Northern State DOTs, and relevant LinkedIn groups. Up to June 26, 2012, a total of 106 responses were received (31 from government agencies and 75 from private entities), among which 41 responses were complete and used for further analysis. The complete survey results, including the survey instrument (questionnaire), summary of survey responses, and a summary of responses are listed as **Appendix B**. The key findings are also presented in Chapter 3.

2.3. Laboratory Investigation

2.3.1. Preliminary Laboratory Investigation

Materials

The carbon steel coupons used in this research were purchased from Metal Samples (Munford, AL) made of Cor-ten B type (UNS number K11430; density: 7.60 g/cm³; chemical composition: C 0.10 – 0.19 %, Cr 0.40 – 0.65 %, Cu 0.25 – 0.40 %, Fe 97.0 – 98.2 %, Mn 0.90 – 1.25 %, P ≤ 0.04 %, Si 0.15 – 0.30 %, S ≤ 0.05 %, V 0.02 – 0.10 %) with the exposed surface area of 2 cm². Sodium chloride (NaCl), magnesium chloride (MgCl₂) and other chemical used were purchased from Fisher Scientific (Pittsburgh, PA). The carbon steel substrates were polished using different grades of SiC sandpaper up to # 1000 and de-ionized (DI) water was used in this study.

The anti-corrosion coating products, Zero Rust Red (Amteco, INC.), Zero Rust Black (Amteco, INC.), Rust Bullet (Rust Bullet LLC.) and Lubra-Seal (Rhomar Industries Inc.) are used as received from the distributor. The spray-on corrosion inhibitors, Krown (Krown Company), Ship-2-Shore (Ship-2-Shore Inc.), Vegetable Oil (Crisco) and Rust Oleum (Rust-Oleum) are also used as received. The salt removers, MR 35 (Krown Company), HoldTight (HoldTight Solutions Inc.), ChlorRid (ChlorRid international Inc.), SaltAway (Salt-Away Product, INC), Soap Water (Softsoap Brand) and Neutro-Wash (Rhomar Industries) are diluted by water as the ratio of 1:10, 1:100, 1:100, 1:521, 1:55, 1:100, respectively.

Corrosion coupon preparation

A copper wire was electrically connected to one surface of each corrosion coupon (e.g., steel). Then this surface and all the other surfaces except the one exposed to electrolyte for corrosion testing were sealed with a thick bulk epoxy resin. After epoxy curing, the unsealed coupon surface was polished on silicon carbide (SiC) papers down to a grit size of 1000 with the aid of a metallographic grinding disc. After polishing, the sample surface was rinsed with tap water and sonicated in de-ionized water.

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) and linear polarization (LP) data were collected using the Gamry Potentiostat with a three-electrode system, including a platinum mesh serving as the counter electrode, a SCE serving as the reference electrode and a coupon sample serving as working electrode. The EIS measurements were taken by polarizing the working electrode at ± 10 mV around its OCP using sinusoidal perturbations with a frequency between 300 KHz and 5 mHz (10 points per decade). The Gamry analysis software was used to plot and fit the EIS data.

In the potentiodynamic weak polarization tests, the coupon was polarized around its corrosion potential (−30 mV to 30 mV/SCE vs. OCP by a direct current (DC) signal at a scan rate of 0.2 mV/s. Polarization resistance (Rp) is defined by the slope of the potential current

density plot at the corrosion potential. Corrosion current (I_{corr}) is calculated from $I_{\text{corr}} = B/R_p$, assuming $B=26$ mV for the steel corrosion.

Screening test

Based on the literature review and survey results, four anti-corrosion coating products (Zero Rust Red, Zero Rust Black, Rust Bullet and Lubra-Seal), four spray-on corrosion inhibitors (Krown, Ship-2-Shore, Vegetable Oil and Rust Oleum) and six salt removers (MR 35, HoldTight, ChlorRid, SaltAway, and Neutro-Wash, each diluted by water to vendor-specified ratios; and Soap Water, diluted by water at 1:55 volume ratio to achieve a viscosity similar to a diluted salt remover solution) were identified and tested. For the screening test of inhibitor products, the corrosion coupons (carbon steel) were immersed in the inhibitor solution for 10 min and then immersed in 30% MgCl_2 solution for 2 hr, and finally the EIS measurements were performed on each corrosion coupons. Similarly, for the screening test of coating products, the coated carbon steel coupons were immersed in 30% MgCl_2 solution for 2 hr before the EIS measurements were performed on each of them. Salt removers are water-like solutions that spray on vehicles/equipment after they have been used for a storm event, so as to remove residual salt and minimize its corrosion to the metal substrate. The coupons were first immersed in 30% MgCl_2 solution for 2 hr and then immersed in the diluted salt remover solution for 10 min. Thereafter, EIS measurements were performed in a 0.1% MgCl_2 solution. After the screening tests, the better performing products were subjected to a two-week test described below, in order to further compare and validate their performance in corrosion protection of steel substrates.

Two-week test

Salt remover procedure:

Two duplicate metal coupons were soaked in 3% wt. MgCl_2 solution for one week, and then washed by a power machine with 1400 psi pressure for 30 seconds. The liquid in the machine consist either the diluted HoldTight or diluted Chlorid solution as a salt remover. Once the power wash was done, coupons were placed back into the same 3% MgCl_2 solution. Repeat the same procedure after another week of soaking; the EIS testing was performed on those coupons in the soaking solution.

Inhibitors procedure:

Two duplicate coupons were soaked for each select inhibitor for 10 min and then placed into 3 wt.% MgCl_2 solution. After two weeks of soaking, EIS measurements were taken for the coupons immersed in the same solution.

Coatings procedure:

Two duplicate coupons were dipped into each select coating for 20 min then wait for 24 hours for the coating to cure. After the coating was cured, the coated coupons were immersed in 3 wt.% MgCl_2 solution. After two weeks of soaking, EIS measurements were taken for the coupons immersed in the same solution.

Wet-dry test

To simulate the field condition occurred in the winter maintenance, three common metals seen in DOT equipment, carbon steel (C1010), Aluminum alloy (Al1100) and stainless steel (SS304L) were selected for the wet-dry tests. Three duplicate coupons were tested for each combination of metal type and exposure condition. First, a metallic coupon was immersed into a 30 wt.% $MgCl_2$ solution for 40 minutes. Then EIS and LP measurements were taken for the coupon, using a Gamry potentiostat. At hour 2, the coupon was taken out and immediately dried in the open air (with relative humidity of approximately 20%) and room temperature for 22 hours. At hour 24, the coupon was immersed into water for 40 minutes, before being placed in a 0.1 wt.% $MgCl_2$ solution and tested for EIS. At hour 26, the coupon was taken out and immediately dried in the open air (with relative humidity of approximately 20%) and room temperature for 22 hours. This forms a 48-hr cycle and each coupon was exposed to a total of 8 cycles. For testing of salt removers (soapy water and HoldTight respectively), at hour 24, instead of being immersed in water for 40 minutes, the metallic coupon was power-washed by the salt remover solution for 30 seconds and then placed in a 0.1 wt.% $MgCl_2$ solution and tested for EIS.

2.3.2. Multi-electrode Array Sensor (MAS) Assessing Metallic Corrosion under Deicer Environments

Sensor fabrication

A total of 12 MAS sensors were assembled in the SwRI laboratory. They were categorized by three sets and each set includes four identical sensors, the probes of which were fabricated with the same material. Three different vehicle component materials, including 1008 carbon steel (CS), 304 stainless steel (SS) and 1100 aluminum (Al) were used as sensor probe materials, with their chemical composition shown in Table 1. The sensors were wire connected to commercial data logger for data acquisition. A366/1008 CS (ASTM A1008 / A1008M - 12) wires were provided by MALIN Company, Inc. (Cleveland, OH). 304 SS wires were obtained from Loos Company. Aluminum wires were 1100 Al (ASTM B209-10) obtained from MALIN Company, Inc. All wires were 1.0 mm in diameter and the same diameter was used for the MAS probe pins.

Table 1. Chemical composition of engineering materials for sensor fabrication

	Si	Fe	Cu	Mn	Zn	C	Ni	Cr	S	P	Al
1100 Al	0.095		0.05-0.20	0.05	0.10						99.00
304 SS	1.0 max	Balance		2.0 max		0.08 max	8.0-10.5	18-20 max	0.03 max	0.045 max	
1008 CS		99	0.2 max	0.6 max		0.08				0.035 max	

The schematic representation of a single MAS configuration is shown in Figure 2. Each sensor includes 9 probes (1.0 mm in diameter) and the center-to-center distance between two adjacent probes is 1.5 mm. The diameter of sensor is approximately 1 cm and

the sensor body is approximately 10 cm length. PTFE tube was used as the sensor jacket and epoxy resin (along with its hardener) was used to fill in the tube and fix the probes. The end of sensors is wired up with military connector to facilitate electrical connection with commercial data acquisition systems.

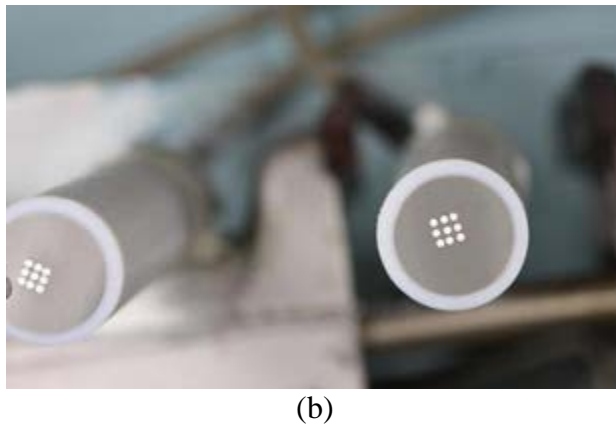
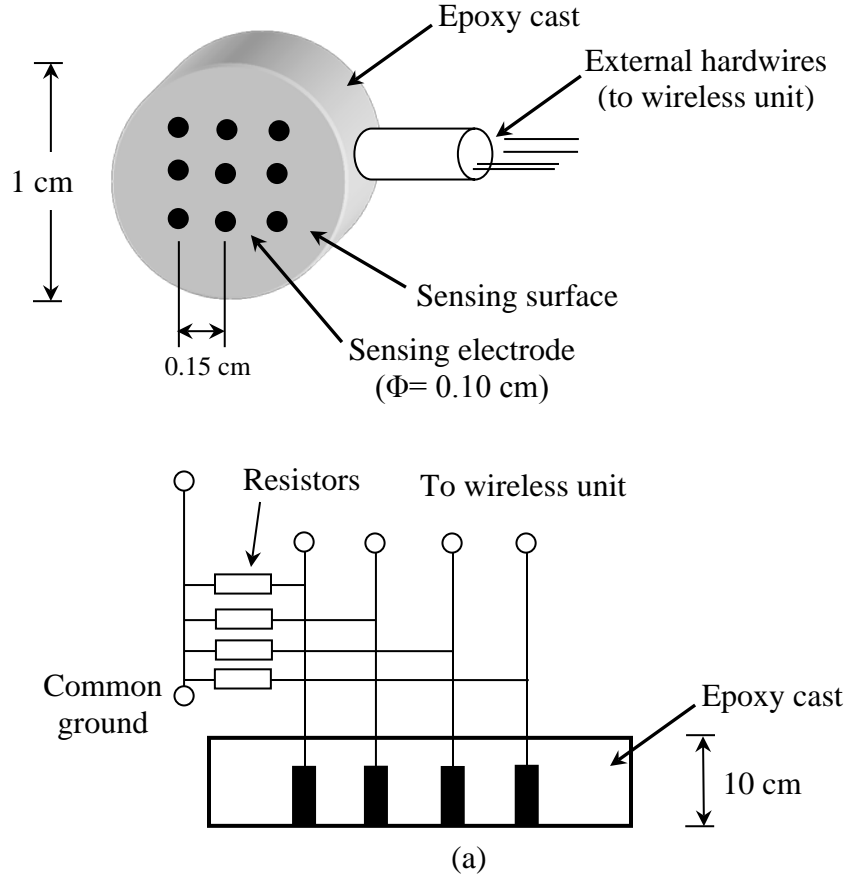


Figure 2. MAS sensor (a) schematic representation and (b) close-up (cross-section) picture.

Cyclic exposure setup

Subsequent to sensor assembly, two environmental exposure tests were conducted. During the tests, the sensors were separated into four groups including one sensor in each set, as shown in Figure 3. The 1st sensor group was used as control with no inhibition approach applied throughout the exposure. The 2nd and 3rd sensor groups were spray applied inhibitor *Krown T40* and *Rust Oleum*, respectively, within each exposure cycle; the 4th sensor group was coated one time with a rust-inhibitive protective coating *Rust Bullet* and then subjected to the test cycles.

It has been found that 80 cycles of SAE J2334 accelerated laboratory test corresponded well with five years of outdoor, on-vehicle testing for steel (Wang et al., 2006). As such, each test cycle was conducted following the SAE J2334 (Rev. Dec. 2003) and consists of three basic stages:

- 1) Humid Stage: 50 °C and 100% humidity, 6 hours in duration
- 2) Salt Application Stage: 15 minutes immersion in the deicer solution conducted at ambient conditions
- 3) Dry Stage: 60 °C and 50% humidity, 17 hours and 45 minutes in duration

The test cycle is repeated daily, i.e., 24 hours per cycle. A total of 8 cycles was performed for each exposure test. Ramp time between the salt application stage and dry stage were part of the dry stage time. Similarly, ramp time between the dry stage (3) and humid stage (1) were part of the humid stage. In the salt application stage, the sensors were subject to an application of salt solution by immersing sensors in salt solution for 15 minutes. For the two exposure tests, two deicer solutions, 2.3% NaCl and 3.0% MgCl₂, respectively, were used for the “salt application stage”. The sensors were re-polished or re-coated after the 1st exposure test and before the 2nd exposure test.

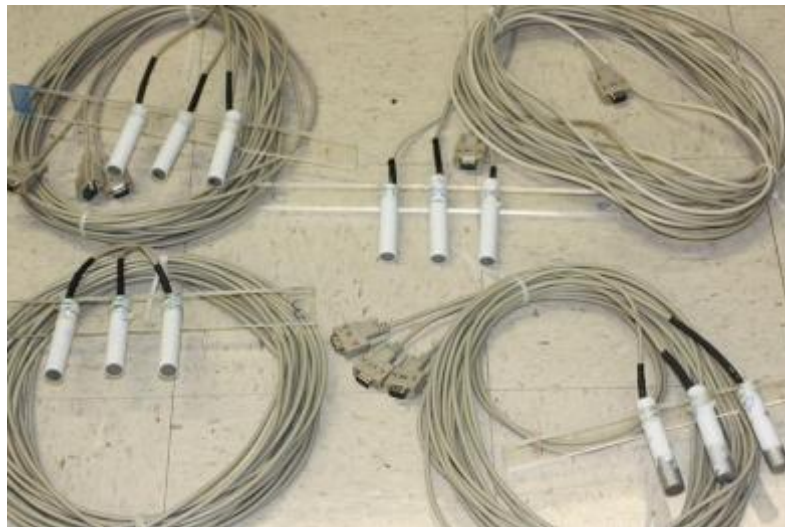


Figure 3. Photographic illustration of the MAS sensors, separated by groups, before environmental exposure

For the 2nd and 3rd sensor groups, a corrosion inhibitor (*Krown T40* and *Rust Oleum* respectively) was applied at 15 minutes after the end of each salt application stage. The chamber hood was manually opened and the inhibitor was sprayed on the surface of the sensor. The amount of inhibitor in each spray covering sensor surface ($\sim 1.0 \text{ cm}^2$) was approximately 0.1 mL. The 4th sensor group was coated one time with *Rust Bullet* (with dry film thickness of 1.45 mm, 1.78 mm, and 1.30 mm for Al, SS, and CS substrates respectively) and then subjected to the test cycles.

A cyclic corrosion chamber from Auto Technology was used for the exposures. The modified SAE J2334 procedure was set up in the PC and used to control the exposure environment automatically whereas the salt application stage and inhibitor application was performed manually. A 100-channel Multichannel Microelectrode Analyzer (MMA) from Scribner Associates, Inc. was used to collect corrosion current density data from probes of each individual MAS, with an acquisition frequency of every 3 minutes.

Figures 4 to 8 photographically demonstrate the MAS sensor groups for the test, test chamber, test setup and different exposure stages, respectively. Immediately after the 8 cyclic exposures, sensor appearance was photographically recorded.



Figure 4. Photographic illustration of sensor setup in the environmental chamber



Figure 5. Photographic illustration of the cyclic corrosion chamber (Humid Stage) and control program

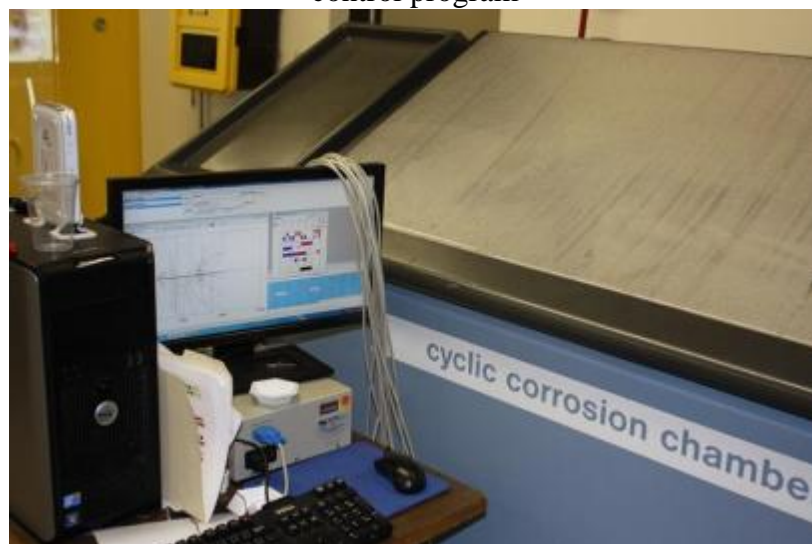


Figure 6. Photographic illustration of the cyclic corrosion chamber (Humid Stage) and MMA data acquisition system

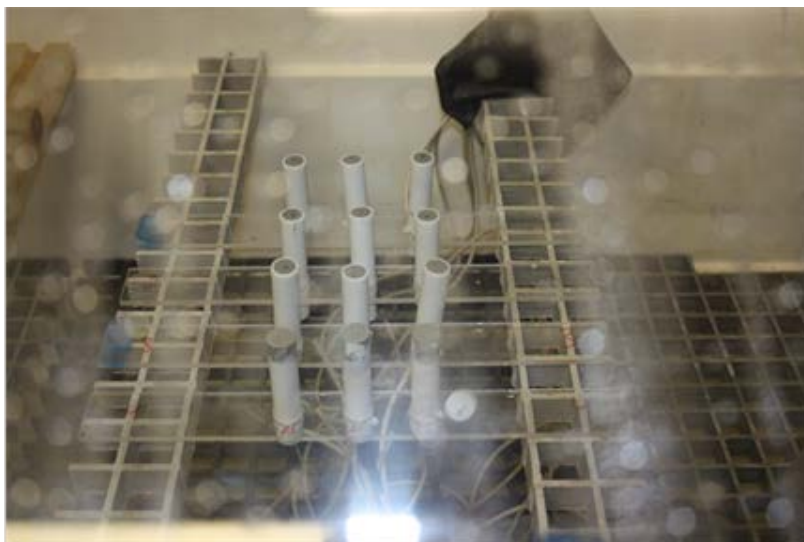


Figure 7. Photographic illustration of sensors during the exposure cycle (Humid Stage)



Figure 8. Photographic illustration of sensors during the exposure cycle (Salt Application Stage)

EIS measurements and 3D laser profilometer scans

After cyclic exposure tests, EIS measurements and 3D laser profilometer scans were conducted for panels made of carbon steel and exposed to the NaCl deicer, as little corrosion occurred on the MAS made of aluminum or stainless steel. To enable reliable EIS measurements, the three-stage exposure environment as described in cyclic exposure tests were reduced to two stages, by combining the humidity stage and the salt application stage into a continuous immersion stage. Only corrosion inhibitors were evaluated with such tools, as little corrosion occurred on the MAS protected by the coating.

The EIS measurements were conducted using a conventional three-electrode system. The working electrode used one of three 10 cm × 10 cm carbon steel panels at a time, each of which featured a working area (exposure area) of approximately 100 cm². Saturated calomel electrode (SCE, Fisher 13-620-52) and platinum mesh served as the reference and counter

electrodes, respectively. During measurements, the SCE was placed very close to the working electrode through a salt bridge. Flat Cell Kits (Model K0235) from Princeton Applied Research was used as the corrosion cell, and a VMP3 Multichannel Potentiostat from Princeton Applied Research was set up for the electrochemical measurements.

For the EIS tests, a total of 8 cycles was conducted for each carbon steel panel. In each cycle, there was a 6-hour continuous immersion in 2.3% NaCl solution followed by an 18-hour dry stage (ambient exposure). In other words, the humidity stage and the salt application stage in the modified SAE J2334 procedure were combined into a 6-hr continuous immersion stage. The inhibitors were sprayed on the exposed specimen area at the beginning of each dry stage. The EIS measurements of each panel were conducted at the end of the immersion stage of 1st, 3rd, and 8th cycles, respectively, using a frequency from 20,000 Hz to 1 mHz and 10 points recorded per decade.

Once the exposure was done, the panels were disassembled from the electrochemical cell and cleaned with acetone immediately. A laser profilometer (Pacific Precision Laboratories, Inc.) and software (ZSCOPE) were used to characterize the corrosion morphology and depth.

2.4. Cost-Benefit Analysis

This study has provided an analysis of the direct costs related to metallic corrosion on DOT equipment fleet (including winter maintenance application equipment) aggravated by the exposure to chloride roadway deicers, as well as an analysis of the direct benefits of mitigating such corrosion. Wherever possible, the analysis utilizes information obtained from the agency survey conducted in this work, as well as information obtained from other studies. When necessary, reasonable assumptions are made to enable quantitative analysis and the assumptions are clearly stated. A general cost-benefit analysis was first conducted for mitigating deicer-related equipment corrosion of an “average agency”, which is followed by a detailed case study for the Washington State DOT (WSDOT).

CHAPTER 3 – RESULTS AND DISCUSSION

3.1. Findings from the Published Literature

A comprehensive literature search was conducted to gather existing research documents that are relevant to the corrosion of metals by chloride salts (the main ingredients of roadway deicers), with a focus on corrosion under neutral pH conditions and under ambient temperature and pressure. This section provides a high-level summary of information from the literature synthesis, which is detailed in this report as **Appendix A**. The literature synthesis includes six chapters, i.e., Corrosion Cost Analysis; Corrosion Mechanisms and Effect of Deicer Corrosion on Metals; Proactive Approaches to Corrosion Prevention; Coatings for Corrosion Protection; Inhibitors for Corrosion Protection; Test Methods and Online Monitoring Techniques for Anti-Corrosion Practices.

From the published literature, it is clear that the corrosion-related deterioration and damage is a major durability concern for assets in many industries including the U.S. military, DOTs, airlines and others. For instance, the cost of metallic corrosion to the U.S. military is estimated to be 10 to 20 billion dollars per year [14]. Maintenance equipment used to deliver, load and apply chemical deicers is subject to aggravated corrosion as a result of extensive exposure to deicers [7]. The corrosion of metals as a result of chemical or electrochemical reaction with their service environment is a spontaneous process, which can compromise the material's integrity and impact assets, environment and people if no measures are taken to prevent or control it.

Chloride-based salts are the main freezing point depressants used in snow and ice control products found in highway maintenance applications and they present a major risk to metals in vehicles and other equipment as well as metals in bridges and other infrastructure. A recent survey of highway maintenance agencies indicated that sodium chloride (NaCl) was the most frequently used deicer followed by abrasives, then magnesium chloride (MgCl_2), agro-based products, calcium chloride (CaCl_2) and others. Less than 25% of the survey respondents used alternative deicers such as potassium acetate (KAc), sodium acetate (NaAc), calcium magnesium acetate (CMA) and potassium formate [8]. In 2007 the U.S. sold approximately 20.2 million tons of NaCl for use in winter road maintenance [9]. The growing use of deicers has raised concerns over their effects on motor vehicles, transportation infrastructure, and the environment [10-13].

Deicer-induced corrosion may affect the performance and service life of metallic components, electrical connections, joint connections, hydraulic systems, bearings, engine components, etc. The costs associated with corrosion to this equipment are substantial and include repair or replacement of corroded parts, premature failure and replacement of worn-out equipment. The corrosion of motor vehicles due to road salts was estimated to cost \$2.8 billion to \$5.6 billion per year. This included the added manufacturing expense for vehicle protection and preventive maintenance along with the cost of owner preventive maintenance and cosmetic-corrosion-related vehicle depreciation [19]. A more recent study estimated the total cost of corrosion to motor vehicles (from road salts as well as other culprits, e.g., marine environment) to be \$23.4 billion per year [20]. On average, the deicer corrosion to each vehicle was estimated to cost \$32 per year [12]. Additionally, the safety of operators and the

traveling public is put at risk by the potential failure of components and/or entire units resulting from corrosion.

The literature review has focused on the metals commonly seen in DOT vehicles and equipment, including: steels, aluminum/aluminum alloys, magnesium alloys, zinc, and cast irons. Different metals have inherently different characteristics and they may differ greatly in their type and extent of corrosion in the service environment. There are a variety of thermodynamic and kinetic factors (e.g., humidity, time of wetness, chloride level, sulfur level, dissolved oxygen, pH, and temperature) that determine the tendency and rate of vehicle corrosion.

There are many forms of corrosion, including: general corrosion and localized corrosion (galvanic corrosion, pitting corrosion, filiform corrosion, poultice corrosion, crevice corrosion, intergranular corrosion, erosion corrosion, stress corrosion cracking - SCC, corrosion fatigue, microbially influenced corrosion, etc.). In a case study conducted by the Western Transportation Institute (WTI), the corrosion of trucks exposed to chloride deicers applied on Montana highways was investigated and significant crevice corrosion between the conjunction of winch frame and truck frame was observed along with filiform corrosion under the coating near frame corners and on brake chambers. Other forms of less significant corrosion on the trucks were observed as well, such as pitting corrosion on the outer surfaces of stainless steel parts and aluminum fuel tanks, galvanic corrosion and SCC in the welding zones [15].

To protect assets (e.g., maintenance equipment) from the negative effects of corrosion, it is important to take countermeasures that would prevent or control the metallic corrosion and minimize the associated costs. The mechanistic knowledge underlying the corrosion and corrosion inhibition processes are essential in the search for more corrosion-resistant materials or other countermeasures. For instance, for metals commonly seen in DOT vehicles and equipment (steels and aluminum alloy), it has been found that $MgCl_2$ tends to cause more corrosion damage than $NaCl$ does in humid condition but $NaCl$ is more corrosive than $MgCl_2$ under dry conditions. This is due to the hygroscopic nature of $MgCl_2$.

The corrosion of metals in equipment can be mitigated through better material selection, improved design, and proactive maintenance practices, both individually and synergistically. For instance, the zinc coating on steel substrates can provide good anti-corrosion performance [16]. The use of alloys to decrease the tensile stress can be helpful in situations where SCC dominates [17]. Taking the requirements of corrosion resistance into consideration at the design stage can significantly mitigate or even avoid the negative impacts of corrosion. Structures designed for resistance to *atmospheric corrosion* should always provide easy drainage from all exposed surfaces. *SCC* can be prevented by substituting a more resistant alloy, removing the tensile stress, or making the environment less aggressive. *Crevice corrosion* can be minimized by proper design of welded joints and gaskets that minimize crevices. Contact between dissimilar metals can lead to *galvanic corrosion* and should be avoided wherever possible. Most of the chloride-based salts on vehicles and equipment can be washed with low pressure water blasting, but salts that have attached and complexed with the metal substrate often cannot be removed with 40,000 psi Ultra High Pressure Water-jetting (UHPWJ). It has been found that frequent washing (with or without salt removers) can reduce the corrosion caused by residuals of roads salts on DOT equipment [18].

The deicer corrosion to DOT equipment and vehicles can also be mitigated through reactive maintenance practices. Coatings and corrosion inhibitors are two important tools in corrosion protection. A wide variety of metallic, polymeric or ceramic coatings and inhibitors (organic compounds, inorganic compounds, polymers, etc.) have shown promising results in reducing the corrosion of metallic substrates. Advances in materials science and nanotechnology have greatly contributed to new and improved corrosion prevention systems. New innovations such as self-repairing coatings and encapsulated inhibitors, capable of protecting metals against corrosion both actively and passively, will become more common when further improvements are made to reduce their cost and improve their performance.

The literature review also identified test methods applicable to assess the risk of deicer corrosion to metals and sensor technologies that could be implemented to enable the online monitoring of such risk.

3.2. Findings from the Survey

A note of caution: The survey responses illustrate either field experience or perspectives by the survey respondents and/or their agencies, which may not always coincide with the actual data from literature or from laboratory or field investigations.

3.2.1. The Problem of Chloride Deicer Corrosion: How Serious Is It?

Deicers mostly exposed to vehicles/equipment

The question posed to survey participants sought feedback on the type of deicers that were mostly exposed to their agency's vehicles and equipment. Table 2 gives the number and percentage of respondents who listed each deicer. The data indicate that four deicers, including salt, pre-wetted salt, sand/salt blend and sodium chloride brine, have been listed as "frequently or very frequently exposed" to vehicles/equipment in this survey. It is interesting to note that only 12.6% of the survey respondents used non-chloride deicers, likely due to the fact that chloride deicers are more available, cheaper or easier to be used for winter maintenance than non-chloride deicers despite their higher risk to vehicles and equipment. Moreover, the survey respondents also indicated that in cold-temperature areas, the use of corrosion-inhibited magnesium chloride (vs. the non-inhibited chloride brines) to pre-wet sand could lead to reduced corrosion risk to vehicles and equipment.

Table 2. Type of deicers mostly exposed to the respondents' agency's vehicles/equipment, showing the frequency of use.

Deicers listed	Frequency	Response Count	Percent of Respondents
Salt	30	38	79%
Corrosion Inhibited Salt	7	35	20%
Pre-wetted Salt	32	40	80%
Sand/Salt Blend	18	35	51.4%
Magnesium Chloride	9	38	23.7%

Corrosion Inhibited Magnesium Chloride	10	37	27%
Calcium Chloride	8	40	20%
Corrosion Inhibited Calcium Chloride	7	34	20.6%
Sodium Chloride Brine	23	38	60.6%
Corrosion Inhibited Sodium Chloride Brine	4	35	11.4%
Non-Chloride Deicers	4	32	12.6%

Annual expenditure on managing the deicer corrosion of vehicles/equipment

The agency survey identified annual expenditures in the current practices of managing deicer-related metallic corrosion in the equipment fleet of responding agencies that report it as being a significant issue. While there are some responses from cities and counties, most responses came from state DOTs in the U.S. Table 3 reports the average estimated cost of corrosion management in six areas as follows: training programs (\$190,938), materials selection (\$320,667), design improvements (\$45,000), corrosion monitoring and testing (\$10,000), proactive maintenance (\$171,424), and reactive maintenance (\$325,000). As such, the total cost of current corrosion management related to deicer exposure is estimated to be \$1,063,029 per year. The coefficient of variance among the six cost items averaged 143%, which is attributed to the inherent diversity in the responding agencies' fleet size, level of deicer exposure and other environmental conditions, rules of practices in corrosion management, etc. Nonetheless, it is assumed that the average cost numbers reported here reflect the current practice by an "average agency" (e.g., a northern state DOT with an average size of fleet asset) [29-33].

Table 3. Annual expenditures of current practices in managing equipment corrosion due to deicer exposure

	Training programs	Materials selection	Design improvements	Corrosion monitoring /testing	Proactive maintenance	Reactive maintenance
No. of Responses	8	15	9	1	14	8
Average	\$190,938	\$320,667	\$45,000	\$10,000	\$171,424	\$325,000
Standard Deviation	\$342,845	\$568,651	\$43,157	NA	\$279,106	\$319,598
Coefficient of Variance	180%	177%	96%	NA	163%	98%

* One estimated value (\$359,942) was incorporated into the survey responses for calculating the average cost of proactive maintenance. This was based on the assumption that 19.6% of the proactive maintenance cost on the WSDOT equipment fleet (\$1,839,118, in 2011 US dollars) can be attributed to the exposure to deicers. The number 19.6% is obtained from an average of survey responses, as detailed later in Table 4.

Risks of deicer corrosion to the equipment fleet

The agency survey also identified the current risks of deicer corrosion to the equipment fleet of responding agencies that report it as being a significant issue, estimated under the current level of corrosion management. Table 4 reports the deicer exposure leads to risks in six areas: an average of 17.3% depreciation in equipment value, an average of 8.5% increased equipment downtime, an average of 11.9% in reduced equipment reliability, an average of 17.3% in reduced equipment service life, an average of 19.6% in increased premature repair and replacement, and an average of 1.5% safety risk due to faulty parts on equipment. Table 5 reports the average estimated cost of equipment corrosion risks in these six areas as follows: \$12,512,227, \$69,167, \$172,000, \$1,127,750, \$118,823, and \$30,000, respectively. As such, the total cost of current corrosion risks related to deicer exposure is estimated to be \$14,050,368 per year. For the reasons mentioned before, the coefficient of variance among the six cost items is high (averaged 125%).

Table 4. Estimated risks of equipment corrosion due to deicer exposure alone

	Depreciation in value	Increased downtime	Reduced reliability	Reduced service life	Increased premature repair and replacement	Safety risk due to faulty parts
No. of Responses	12	13	9	12	7	4
Average	17.3%	8.5%	11.9%	17.3%	19.6%	1.5%
Standard Deviation	12.6%	8.3%	8.7%	12.6%	12.2%	1.0%
Coefficient of Variance	73%	98%	74%	73%	62%	67%

Table 5. Annual costs of estimated equipment corrosion risks due to deicer exposure

	Depreciation in value	Increased downtime	Reduced reliability	Reduced service life	Increased premature repair and replacement	Safety risk due to faulty parts
No. of Responses	9	6	5	4	5	1
Average	\$12,512,227	\$69,167	\$172,000	\$1,127,750	\$139,224	\$30,000
Standard Deviation	\$27,053,553	\$94,943	\$205,597	\$1,121,133	\$72,729	NA
Coefficient of Variance	216%	137%	120%	99%	52%	NA

* One estimated value (\$29,355,047) was incorporated into the survey responses for calculating the average cost of equipment value depreciation. One estimated value (\$246,118) was incorporated into the survey responses for calculating the average cost of increased premature repair/replacement. These two values were calculated based on the WSDOT historical data, and the calculations are detailed later.

3.2.2. Symptoms of Chloride Deicer Corrosion

Metallic corrosion on types of equipment and components

Users were asked to rank the risk of metallic corrosion to the types of equipment the respondents' agency owns and the results were listed in Table 6. From the average number of severity (ignore N/A responses and count those very low as 1, low as 2, moderate as 3, high as 4, very high as 5) listed in Table 6, it can be observed that chloride deicers pose the most significant risk of metallic corrosion to dump trucks (4.1) followed by liquid deicer applicators (3.7), hoppers (3.6), front end loaders (3.5) and supervisor trucks or crew pickups (3.0). Graders (2.5) have the least risk of metallic corrosion.

Users were also asked to rank the risk of chloride deicers to various components of their agency's vehicles/equipment and the results were listed in Table 7. From the data shown in Table 7, 65 % of respondents agree bracket and supports have a relatively or very high risk due to chloride deicers, 65% of respondents agree brake drums and disks have a relatively or very high risk due to chloride deicers and 92.5% of respondents agree that electrical wiring have a relatively or very high risk due to chloride deicers. The results also have showed that fittings (65.0%), frames (75.0%), wheels (64.1%), granular hopper (66.7%), spreader auger (62.1%), spreader chute (71.1%) and hydraulic systems/pumps/hoses/cylinders/valves (63.1%) have a relatively or very high risk of corrosion by ranking of respondents due to the chloride deicers. From the average number of severity listed in Table 3, electrical wiring was identified to have the highest risk to suffer deicer corrosion (4.5), followed by Frames (4.0), Brackets and supports (3.9), Brake air cans (3.9), Fittings (3.9), Spreader chute (3.9), etc. Liquid storage tanks have the lowest risk to deicer corrosion (2.8). This data shows that most of the parts of vehicles and equipment are very vulnerable to corrosion that is caused by chloride deicers.

Table 6. Ranking the risk of metallic corrosion to the types of equipment the respondents' agency owns.

Equipment listed	Not Applicable	Very Low	Low	Moderate	High	Very High	Average No. of severity (response count)
Dump trucks	6.4% (3)	4.3% (2)	4.3% (2)	14.9% (7)	21.3% (10)	48.9% (23)	4.1 (47)
Liquid deicer applicators	2.3% (1)	4.5% (2)	13.6% (6)	25.0% (11)	20.5% (9)	34.1% (15)	3.7 (44)
Hoppers	7.0% (3)	7.0% (3)	9.3% (4)	27.9% (12)	23.3% (10)	25.6% (11)	3.6 (43)
Front end loaders	4.5% (2)	4.5% (2)	15.9% (7)	25.0% (11)	25.0% (11)	25.0% (11)	3.5 (44)
Supervisor trucks or crew pickups	2.1% (1)	6.4% (3)	25.5% (12)	36.1% (17)	23.4% (11)	6.4% (3)	3.0 (47)
Graders	17.8% (8)	15.6% (7)	24.4% (11)	28.9% (13)	8.9% (4)	4.4% (2)	2.5 (45)

Table 7. Ranking the risk of chloride deicers to various components of the agency's vehicles/equipment.

Components	Very low	low	Moderate	high	Very High	Average No. of severity (response count)
Brackets and supports	2.5% (1)	2.5% (1)	27.5% (11)	32.5% (13)	32.5 (13)	3.9 (40)
Brake drums and disks	5.0% (2)	7.5% (3)	20.0% (8)	35.0% (14)	30.0% (12)	3.8 (40)
Brake air cans	2.5% (1)	7.5% (3)	20.0% (8)	32.5% (13)	35.0% (14)	3.9 (40)
Brake lines	7.5% (3)	15.0% (6)	17.5% (7)	30.0% (12)	25.0% (10)	3.5 (40)
Bumpers	5.0% (2)	17.5% (7)	37.5% (15)	22.5% (9)	12.5% (5)	3.2 (40)
Body panels	2.5% (1)	7.5% (3)	37.5% (15)	35.0% (14)	17.5% (7)	3.6 (40)
Electrical wiring	0.0% (0)	0.0% (0)	7.5% (3)	40.0% (16)	52.5% (21)	4.5 (40)
Engines and drive train components	2.5% (1)	10.0% (4)	47.5% (19)	22.5% (9)	17.5% (7)	3.4 (40)
Exhaust systems/Mufflers	2.5% (1)	2.5% (1)	42.5% (17)	32.5% (13)	17.5% (7)	3.6 (40)
Fittings	0.0% (0)	5.0% (2)	27.5% (11)	35.0% (14)	30.0% (12)	3.9 (40)
Frames	2.5% (1)	0.0% (0)	20.0% (8)	47.5% (19)	27.5% (11)	4.0 (40)
Fuel tanks	0.0% (0)	12.5% (5)	35.0% (14)	35.0% (14)	17.5% (7)	3.6 (40)
Radiators	0.0% (0)	10.0% (4)	50.0% (20)	20.0% (8)	17.5% (7)	3.5 (40)
Transmission housings	5.0% (2)	22.5% (9)	30.0% (12)	25.0% (10)	15.0% (6)	3.2 (40)
Trim	5.1% (2)	23.1% (9)	41.0% (16)	15.4% (6)	10.3% (4)	3.0 (39)
Wheels	5.1% (2)	12.8% (5)	15.4% (6)	43.6% (17)	20.5% (8)	3.6 (39)
Granular hopper	19.4% (7)	5.6% (2)	2.8% (1)	30.6% (11)	36.1% (13)	3.6 (36)
Spreader auger	8.1% (3)	16.2% (6)	10.8% (4)	24.3% (9)	37.8% (14)	3.7 (37)
Spreader chute	5.3% (2)	10.5% (4)	7.9% (3)	31.6% (12)	39.5% (15)	3.9 (38)
Spreader disc	18.4% (7)	15.8% (6)	10.5% (4)	21.1% (8)	26.3% (10)	3.2 (38)
Spray bar	15.8% (6)	15.8% (6)	5.3% (2)	31.6% (12)	23.7% (9)	3.3 (38)
Liquid storage tanks	28.9% (11)	18.4% (7)	13.2% (5)	13.2% (5)	21.1% (8)	2.8 (38)
Plow blades/cutting edges	13.2% (5)	23.7% (9)	15.8% (6)	23.7% (9)	18.4% (7)	3.1 (38)
Hydraulic systems/pumps/hoses/cylinders/valves	5.3% (2)	7.9% (3)	21.1% (8)	36.8% (14)	26.3% (10)	3.7 (38)

Common types of corrosion-prone material and their respective forms of corrosion

The survey respondents were also surveyed for the corrosion-prone material seen in their agency's equipment fleet and the results are summarized in Table 8. From Table 8, it can be obtained that the cast irons have the most serious general or uniform corrosion (81.3%) followed by carbon steels (73.5%), composites (68.8%) and magnesium alloys (68.2%). On the other hand, aluminum alloys and stainless steels have the most serious localized corrosion (50%) followed by metallic glass (43.8%) and metallic coatings (40.0%).

Table 8. The common types of corrosion-prone material and their respective forms of corrosion seen in respondents' agency's vehicles/equipment exposed to chloride deicers.

Materials	General or uniform corrosion	Localized corrosion	Response count (*)
Cast irons	81.3% (26)	21.9% (7)	32
Aluminum alloys	55.9% (19)	50.0% (17)	34
Magnesium alloys	68.2% (15)	36.4% (8)	22
Copper and copper alloys	67.9% (19)	35.7% (10)	28
Carbon steels	73.5% (25)	32.4% (11)	34
Stainless steels	50.0% (12)	50.0% (12)	24
Metallic coatings	64.0% (16)	40.0% (10)	25
Metallic glass	56.3% (9)	43.8% (7)	16
Composites	68.8% (11)	31.3% (5)	16

* Some respondents selected both forms of corrosion.

3.2.3. Best Practices or Products for Managing Chloride Deicer Corrosion

Users were asked to give the effective methods of assessing corrosion resistance of parts prior to installation or methods of assessing corrosion performance of parts installed in vehicles/equipment. A total of 51 responses were received and many of the practices to prevent deicers corrosion have been identified as: “make as many components from stainless steel as possible”, “replace with stainless steel or poly wherever possible” and “the use of stainless steel couplers”. Those responses suggest that despite its high cost, stainless steel is a most recognized material to use for parts prone to chloride deicer corrosion. Other successful ways or recommendations for corrosion prevention include: washing vehicles/equipment regularly, powerful washing of winter application equipment after use, using zinc anodes in solution tanks, and mounting electrical junction blocks in cab.

Users were also asked to provide the brand name and vendor of coatings, salt removers, corrosion inhibitors, or other products their agency have used in reducing deicer corrosion. We have got 38 responses and the best products that this survey identified for corrosion prevention are four anti-corrosion coating products (Zero Rust Red, Zero Rust Black, Rust Bullet and Lubra-Seal), four spray-on corrosion inhibitors (Krown, Ship-2-Shore,

Vegetable Oil and Rust Oleum), and six salt removers (MR 35, HoldTight, ChlorRid, SaltAway, Soap Water and Neutro-Wash).

3. 3. Findings from the Preliminary Lab Investigation

3.3.1. Screening Test Results

Electrochemical impedance spectroscopy (EIS) provides useful information on interfaces and thus was used to shed light on the microstructural properties of the coupon surfaces used in this study. The complex impedance of the surface-electrolyte interfaces depends on the frequency of the externally imposed alternating current polarization signal, allowing the representation of the system with an equivalent circuit typically consisting of resistors and capacitors. For this study, the equivalent circuit shown in Figure 9 was used to evaluate the level of corrosion protection offered by various coatings including anti-corrosion coating, corrosion inhibitors and salt removers on coupon surfaces. Constant phase elements (Q) instead of capacitances were used in all fittings. Such modification is obligatory when the phase angle of capacitor is different from -90° . The obtained parameters are given in Table 9, Table 10 and Table 11 where R_1 and Q_1 are the resistance and capacitance of coating characteristic of its pore network structure (the coating-electrolyte interface inside the coating) and R_2 and Q_2 are the corrosion resistance of the carbon steel (coupon) and the double layer capacitance on the steel surface (the steel-electrolyte interface), respectively. R_0 is the solution resistance between the reference electrode and the working electrode (coated carbon steel), which depends not only on the resistivity of electrolyte (ionic concentration, type of ions, temperature, etc.) but also on the geometry of the area in which current is carried. R_0 is not related to the property of coating layers and is not of too much concern, whereas n_1 and n_2 are the fitting coefficient for Q_1 and Q_2 , respectively, in which the number “1” is the perfect fit of a capacitor and the number “0” is the worst fit. From Table 5, it was observed that anti-corrosion coating products could greatly increase the coating resistance R_1 by 3835-21653 times and reduce the coating capacitance Q_1 by 13470-66100 times for four anti-corrosion coating products (Zero Rust Red, Zero Rust Black, Rust Bullet and Lubra-Seal), indicating reduced coating porosity and improved barrier performance for corrosion protection of the carbon steel substrate. It was also observed that the anti-corrosion product can significantly increase the charge transfer resistance R_2 by $1.03 \times 10^6 \sim 9.74 \times 10^{11}$ times and reduce the double layer capacitance Q_2 by 7~ 392 times, indicating enhanced corrosion resistance of the steel at the steel-electrolyte interface [24, 25]. However, the situations are totally different for spray-on corrosion inhibitors and salt removers (shown in Table 6 and Table 7). From Table 10 and Table 11, it could be observed that the inhibitors/salt removers considerably increased the charge transfer resistance (R_2 , 192~5122 times) and coating resistance (R_1) just increased slightly (1.4 ~ 21.8 times). It is interesting to point out that both the coating capacitance (Q_1) and the double layer capacitance (Q_2) increased if the inhibitors/salt removers are used, indicating the corrosion mechanism is complicated when the inhibitors/salt removers are added. Moreover, Table 9 to Table 11 also provided the values of open circuit potential (OCP) and Warburg impedance (W_1); and such data are less reliable indicators of corrosion protection yet shed light on the corrosion inhibition mechanism and the water diffusivity within the coating or inhibitor layer, respectively.

Furthermore, the products (anti-corrosion products, inhibitors and salt removers) with better corrosion efficiency were identified using the EIS data shown in Table 9, Table 10 and Table 11. The screening test results of EIS show that the anti-corrosion products, Rust Bullet and Lubra-Seal have the best anti-corrosion properties. Inhibitors, Krown and Rust Oleum and salt removers, HoldTight and ChlorRid, also exhibited good anti-corrosion properties.

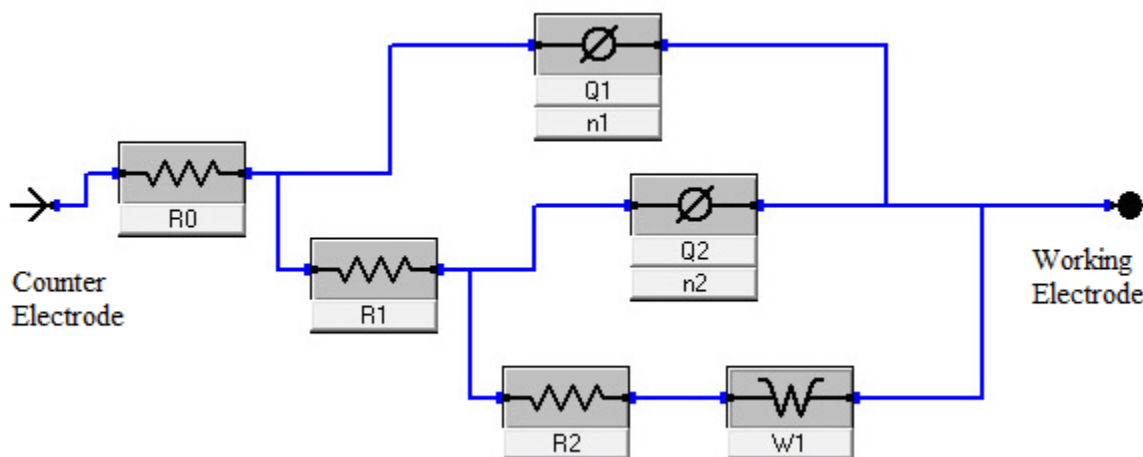


Figure 9. Equivalent circuit used for fitting impedance spectra.

Table 9. Parameters of the equivalent circuits from four anti-corrosion coating products (Zero Rust Red, Zero Rust Black, Rust Bullet and Lubra-Seal) after soaked in the inhibitors for two hours then soaked ten minutes in a 30% MgCl_2 solution.

Coating product	$W_1(\text{mS cm}^{-2})$	$R_1 (\Omega \cdot \text{cm}^2)$	$R_2 (\Omega \cdot \text{cm}^2)$	$Q_1 (\text{F} \cdot \text{cm}^{-2})$	$Q_2 (\text{F} \cdot \text{cm}^{-2})$	OCP (V)
Control	2.05E -7	1.21E + 03	1.15E + 05	4.27E - 06	2.60E - 09	-0.648
Zero Rust Red	3.53E -6	2.62E + 08	1.19E + 11	7.82E - 11	3.71E - 11	-0.444
Zero Rust Black	2.26E -4	3.18E + 07	1.12E + 17	6.46E - 11	2.55E - 11	-0.752
Rust Bullet	1.53E -4	1.24E + 08	8.16E + 16	1.91E - 10	6.63E - 12	-0.640
Lubra-Seal	2.68E -5	4.64E + 06	5.14E + 16	3.17E - 10	3.72E - 10	-0.638

Table 10. Parameters of the equivalent circuits from four spray-on corrosion inhibitors (Krown, Ship-2-Shore, Vegetable Oil and Rust Oleum) after soaked in the inhibitors for ten minutes then soaked two hours in a 30% MgCl_2 solution.

Corrosion inhibitor	$W_1 (\text{mS cm}^{-2})$	$R_1 (\Omega \cdot \text{cm}^2)$	$R_2 (\Omega \cdot \text{cm}^2)$	$Q_1 (\text{F} \cdot \text{cm}^{-2})$	$Q_2 (\text{F} \cdot \text{cm}^{-2})$	OCP (V)
Control	2.05E-7	1.21E + 03	1.15E + 05	4.27E - 06	2.60E - 09	-0.648
Krown	6.38E -8	2.64E + 04	2.21E + 07	4.75E - 09	4.68E - 07	-0.485
Ship-2-Shore	4.74E-7	1.65E + 03	3.70E + 08	5.67E - 07	6.17E - 06	-0.492
Vegetable Oil	1.78E-8	2.83E + 03	3.36E + 08	2.41E - 04	8.69E - 04	-0.655
Rust Oleum	1.25E-8	3.49E + 03	5.89E + 08	2.02E - 04	8.82E - 04	-0.649

Table 11. Parameters of the equivalent circuit from six salt removers (MR 35, HoldTight, ChlorRid, SaltAway, Soap Water and Neutro-Wash). The coupons have been soaked in 30% MgCl_2 solution for two hours then soaked in diluted salt remover solution for ten minutes.

Salt remover	$W_1 (\text{mS cm}^{-2})$	$R_1 (\Omega \cdot \text{cm}^2)$	$R_2 (\Omega \cdot \text{cm}^2)$	$Q_1 (\text{F} \cdot \text{cm}^{-2})$	$Q_2 (\text{F} \cdot \text{cm}^{-2})$	OCP (V)
Control	2.05E-7	1.21E + 03	1.15E + 05	4.27E - 06	2.60E - 09	-0.648
MR 35	3.48E-6	6.75E + 02	3.79E + 13	1.86E - 04	2.82E - 03	-0.482
HoldTight	2.25E-6	1.72E + 03	4.99E + 15	5.28E - 04	1.73E - 02	-0.473
ChlorRid	1.04E-5	1.76E + 03	9.66E + 14	5.35E - 04	1.45E - 03	-0.516
SaltAway	7.69E-7	2.92E + 03	4.26E + 11	9.60E - 04	2.03E - 03	-0.458
Soap Water	2.07E-7	2.13E + 03	1.96E + 11	1.16E - 04	1.21E - 04	-0.338
Neutro-Wash	1.38E-10	1.05E + 03	5.11E + 12	7.11E - 04	8.52E -03	-0.651

3.3.2. Two-Week Test Results

Based on literature review, survey and screening test results, the EIS measurements of corrosion coupons were conducted after two weeks of continuous immersion in a 3% MgCl_2 solution. For the evaluation of corrosion inhibitors or salt removers, the 10-min immersion of

corrosion coupons in inhibitor solution or salt remover solution was conducted on a weekly basis to simulate the proactive maintenance of DOT equipment/vehicles. The test results are shown in Figure 10 - Figure 12 and Table 12 – Table 14.

Figure 10, Figure 11 and Figure 12 present the Nyquist diagrams of the steel coated by ZRust Bullet, soaked in Krown inhibitor solution and soaked in HoldTight salt remover solution after 14-day immersion 3 wt.% MgCl_2 solutions, respectively. Both the experimental data and simulation data (according to the equivalent circuit presented in Figure 9) are given. The obtained parameters are given in Table 12, Table 13, and Table 14, where R_1 and Q_1 are the resistance and capacitance of coating characteristic of its pore network structure (the coating-electrolyte interface inside the coating), and R_2 and Q_2 are the corrosion resistance of the steel and the double layer capacitance on the steel surface (the steel-electrolyte interface) respectively. A collective examination of the corrosion resistance in steel-electrolyte interface (R_2) from the two-hour screening test (Table 9, Table 10, and Table 11) and from the two-week test (Table 12, Table 13, and Table 14) reveal that with the use of coatings, inhibitors and salt removers, the anti-corrosion properties of the steel substrate were greatly improved. A durable protection layer formed on the surface of coupons when the suitable coating (ZRust Bullet), inhibitor (Krown) and salt removers (HoldTight and ChlorRid) were used and these products showed outstanding performance in corrosion protection.

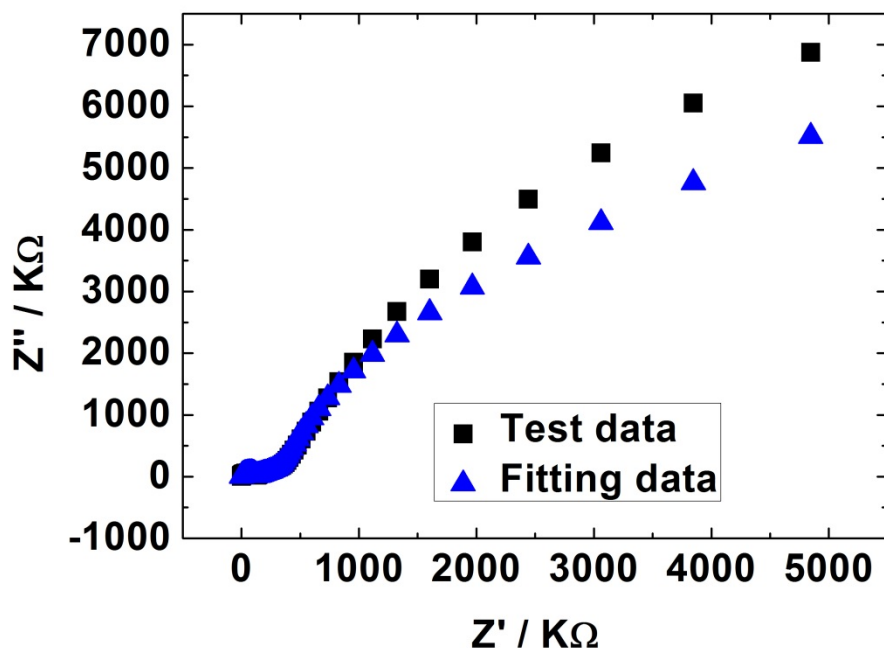


Figure 10. EIS Nyquist diagrams for coupons soaked in ZRust Bullet coating solution for 20 minutes, and then waiting for 24 hours for the coatings to cure. After that, the coupon was soaked two weeks in a 3% MgCl_2 solution. The black points are test data and blue points are simulation data.

Table 12. Parameters of the equivalent circuits from two anti-corrosion coating products (ZRust Bullet and Lubra-Seal) after soaked two weeks in a 3 % MgCl_2 solution.

Coating products	$R_0 (\Omega \cdot \text{cm}^2)$	$R_1 (\Omega \cdot \text{cm}^2)$	$R_2 (\Omega \cdot \text{cm}^2)$	$Q_1 (\text{F} \cdot \text{cm}^{-2})$	$Q_2 (\text{F} \cdot \text{cm}^{-2})$
Rust Bullet	40.30	1.25E + 09	2.58E + 21	3.21E - 10	1.06E - 10
Lubra-Seal	3.974	3.33E + 06	9.76E + 15	3.16E - 07	4.95E - 11

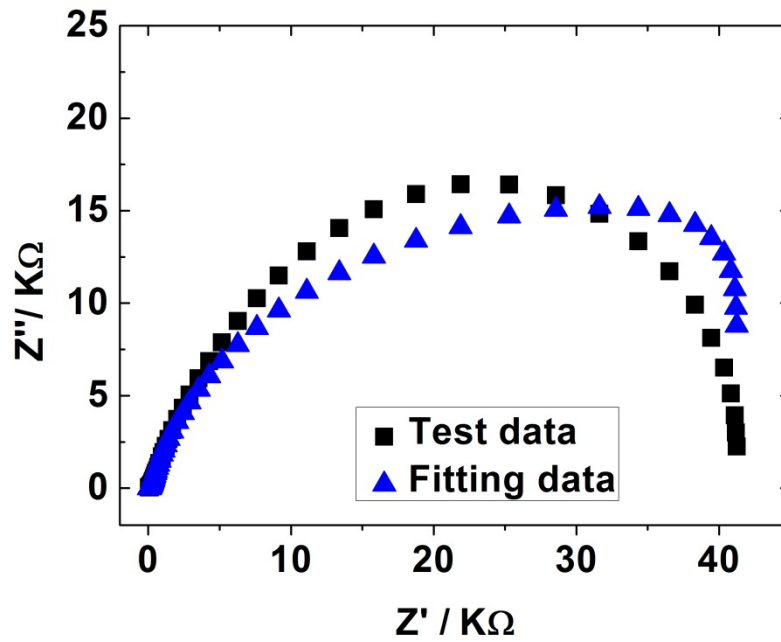


Figure 11. EIS Nyquist diagrams for coupons soaked in Krown inhibitor solution for 10 minutes. After that, the coupon was soaked two weeks in a 3% MgCl_2 solution. The black points are test data and blue points are simulation data.

Table 13. Parameters of the equivalent circuits from two spray-on corrosion inhibitors (Krown and Rust Oleum) after soaked in the inhibitors for ten minutes then soaked two weeks in a 3% MgCl_2 solution.

Corrosion inhibitors	$R_0 (\Omega \cdot \text{cm}^2)$	$R_1 (\Omega \cdot \text{cm}^2)$	$R_2 (\Omega \cdot \text{cm}^2)$	$Q_1 (\text{F} \cdot \text{cm}^{-2})$	$Q_2 (\text{F} \cdot \text{cm}^{-2})$
Krown	66.51	2.48E + 04	5.83E + 09	9.25E - 06	3.58E - 05
Rust Oleum	14.47	1.20E + 03	2.72E + 07	3.36E - 08	1.21E - 05

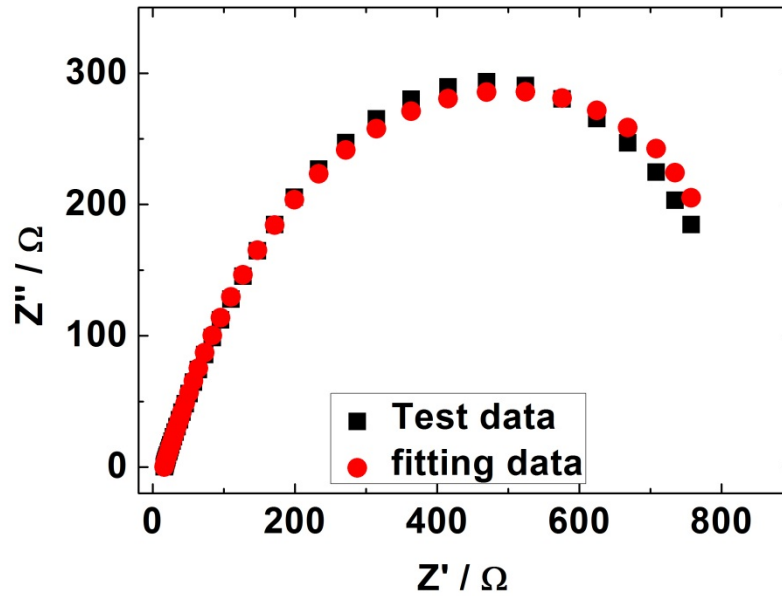


Figure 12. EIS Nyquist diagrams for coupons soaked in HoldTight solution for 10 minutes. After that, the coupon was soaked two weeks in a 3% MgCl_2 solution. The black points are test data and red points are simulation data.

Table 14. Parameters of the equivalent circuit from two salt removers (HoldTight and ChlorRid). The coupons have been soaked in a diluted salt remover solution for ten minutes and then soaked in a 3 % MgCl_2 solution for two weeks.

Salt remover	$R_0 (\Omega \cdot \text{cm}^2)$	$R_1 (\Omega \cdot \text{cm}^2)$	$R_2 (\Omega \cdot \text{cm}^2)$	$Q_1 (\text{F} \cdot \text{cm}^2)$	$Q_2 (\text{F} \cdot \text{cm}^2)$
HoldTight	13.38	1.24E + 03	6.67E + 17	2.02E - 03	3.62E - 02
ChlorRid	19.04	1.22E + 03	2.56E + 17	1.57E - 03	2.34E - 02

3.3.3. Wet-dry test results

To simulate the real field condition in winter maintenance practice, the wet-dry tests have been explored to investigate the anti-corrosion properties of salt removers. In this study, HoldTight, a kind of salt remover with the best anti-corrosion behavior through survey, 2-hour screening test and 2-week long-term test, has been selected to do the wet-dry test using three different metals coupon, carbon steel (C1010), aluminum alloy (A11100) and stainless steel (SS304L). Three carbon steel (or aluminum alloy, stainless steel) coupons firstly dipped into a 30% MgCl_2 solution for 40 minutes and the EIS and LP tests were taken, and then the coupons were dried in the air for 22 hours. After 30-second power washing with soapy water

and *HoldTight* solution (or 40-minute immersion in water), the three coupons are dipped in 30% MgCl_2 solution for 40 minutes and then the EIS and LP tests were taken again. The total 8 cycles (up to 16 days) have been taken during this process and the EIS and LP data are collected from a Gamry potentiostat.

Based on the equivalent circuit presented in Figure 9, the charge transfer resistance (R_2), which is related to the metal-electrolyte interface, has been recorded. Figure 13, Figure 14, Figure 16, Figure 17, Figure 19 and Figure 20 show the relationship between the charge transfer resistance and the days of the wet-dry test whereas Figure 15, Figure 18 and Figure 21 present the relationship between the polarization resistance (R_p) and the days of the wet-dry test. From the change of charge transfer resistance and polarization resistance shown in Figure 13 – Figure 21, the following observation can be obtained: with the use of salt remover, the charge transfer resistance and polarization resistance are significantly enhanced in 30% MgCl_2 solution for carbon steel and stainless steel. For carbon steel coupon washed by salt remover, it will take 9 days to decrease the charge transfer resistance to the similar values collected from the coupons washed by water or soapy water (shown in Figure 13), but for stainless steel coupon washed by salt remover, it will take 13 days to decrease the charge transfer resistance to the similar values collected from the coupons washed by water or soapy water (shown in Figure 19). These data imply that once active corrosion of metals started, the benefits of simply power-washing in reducing the corrosion rate of metals would diminish. This seems to contradict with previous research by Hara et al. [34], who reported that high-pressure (2 – 4 MPa, i.e., 290 – 580 psi) washing with water alone effectively suppressed the deicing salt (mainly NaCl) corrosion of weathering steel bridges over a three-year field investigation. Such inconsistency may be attributed to the difference between weathering steel and carbon steel and the difference between laboratory and field exposure conditions.

The polarization resistances collected from carbon steel and stainless steel washed by salt remover *HoldTight* are much larger than that washed by water or soapy water (Figure 15 and Figure 21), indicating significant benefits of using *HoldTight*. However, the charge transfer resistance and the polarization resistance collected from aluminum alloy coupons washed by salt remover were similar to the values collected from the coupons washed by water or soapy water, indicating little benefits of using *HoldTight* over the test duration.

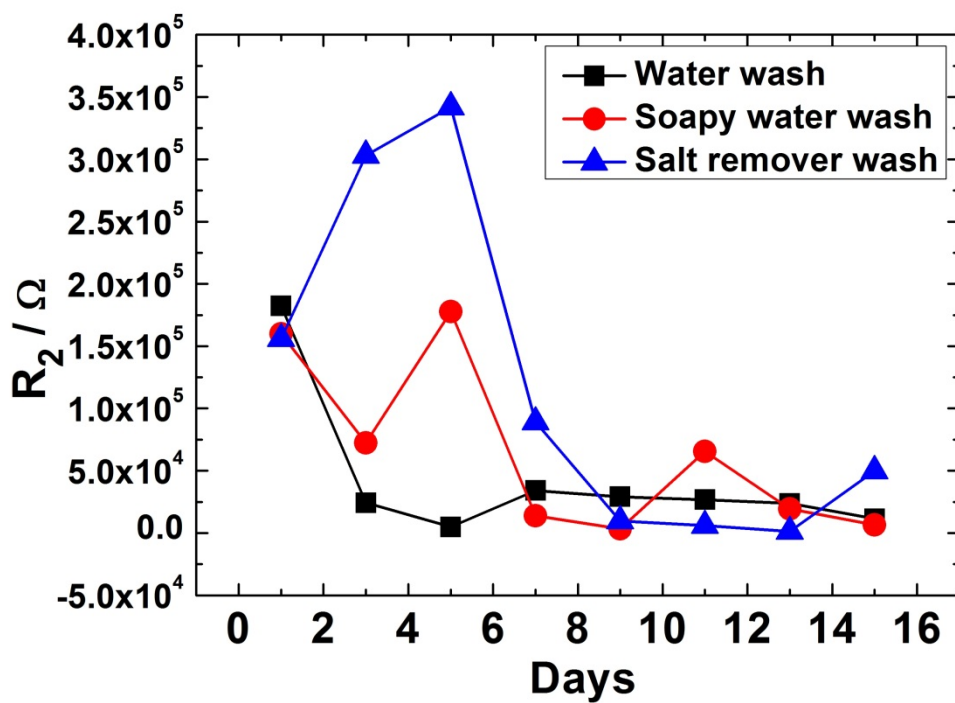


Figure 13. The relationship between charge transfer resistance (R_2) and the days from carbon steel coupons (C1010) in a 30 wt.% $MgCl_2$ solution.

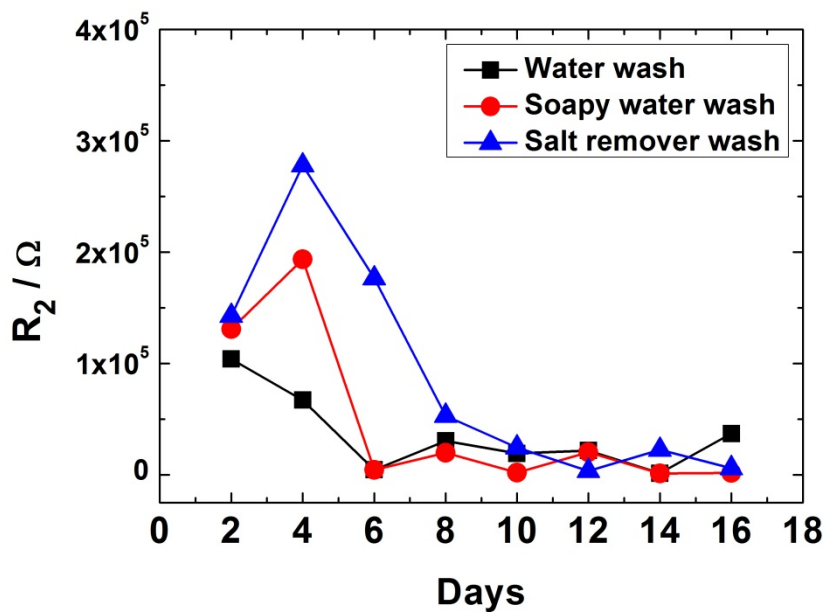


Figure 14. The relationship between charge transfer resistance (R_2) and the days from carbon steel coupons (C1010) in a 0.1 wt.% $MgCl_2$ solution.

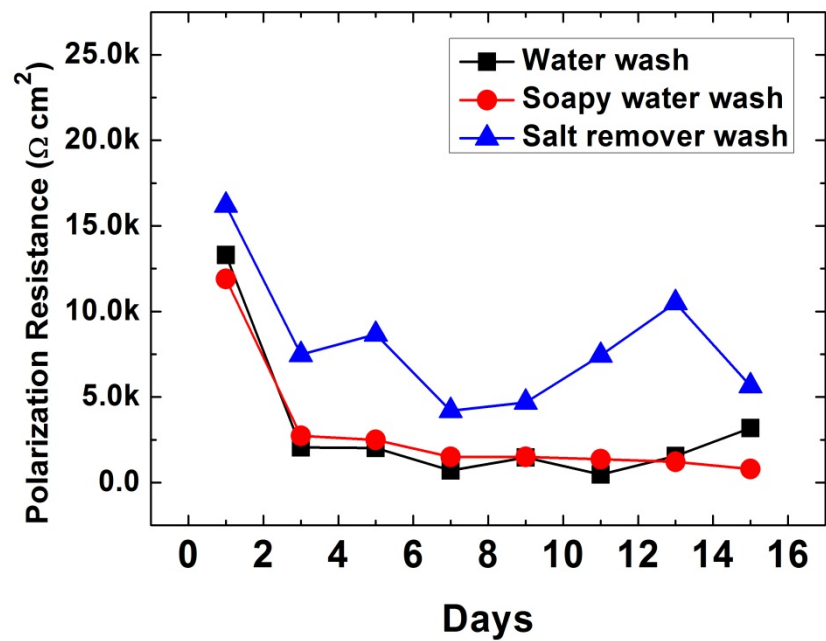


Figure 15. Temporal evolution of polarization resistance of carbon steel coupons (C1010) in a 30 wt.% MgCl_2 solution.

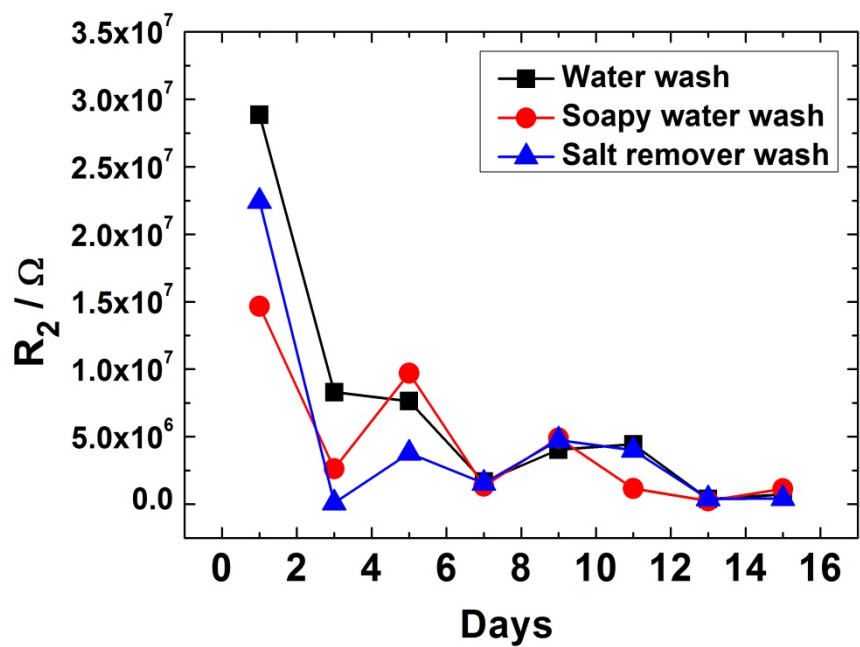


Figure 16. The relationship between charge transfer resistance (R_2) and the days from aluminum alloy coupons (A11100) in a 30 wt.% MgCl_2 solution.

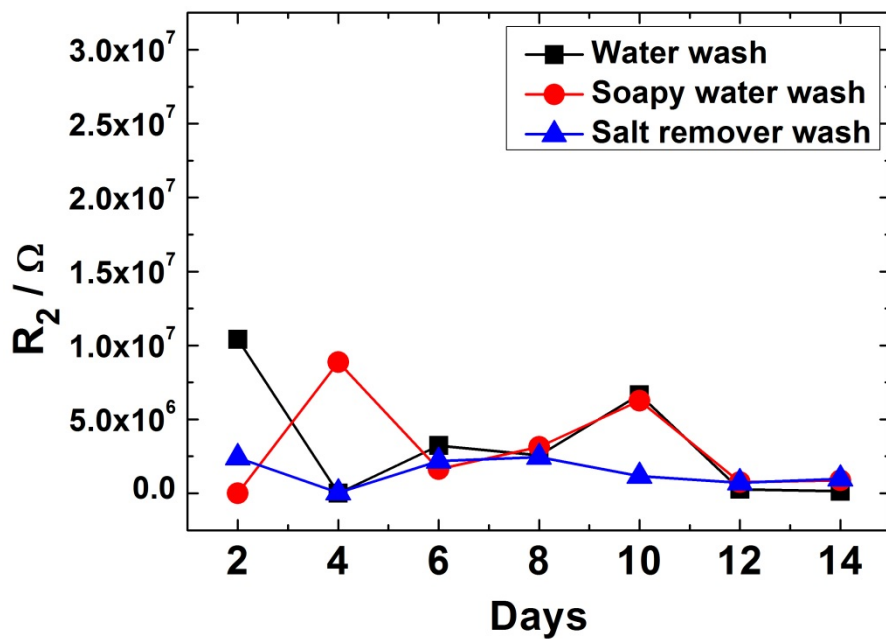


Figure 17. The relationship between charge transfer resistance (R_2) and the days from alluminum alloy coupons (A11100) in a 0.1 wt.% $MgCl_2$ solution.

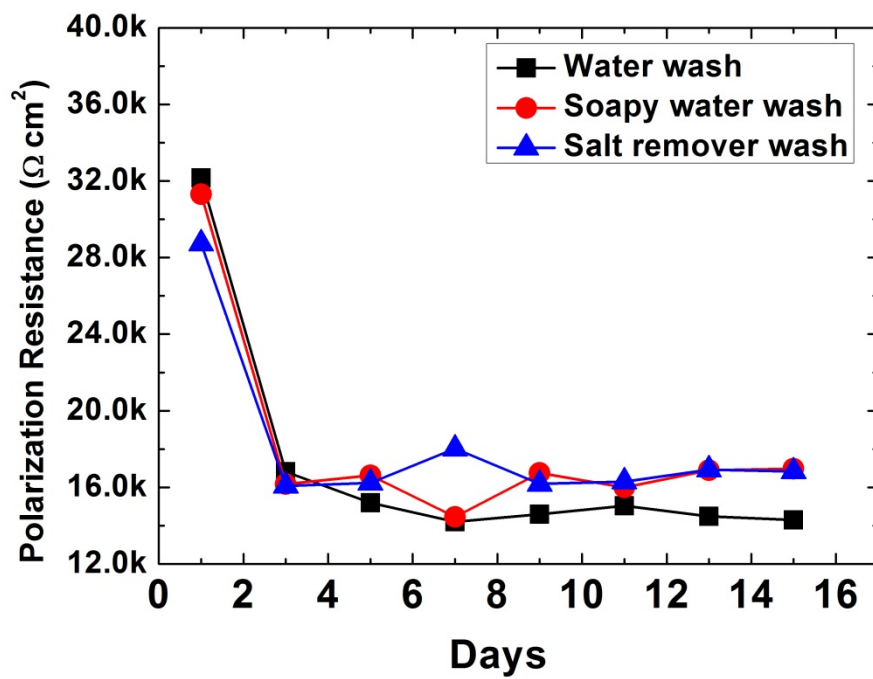


Figure 18. Temporal evolution of polarization resistance of aluminum alloy coupons (A11100) in a 30 wt.% $MgCl_2$ solution.

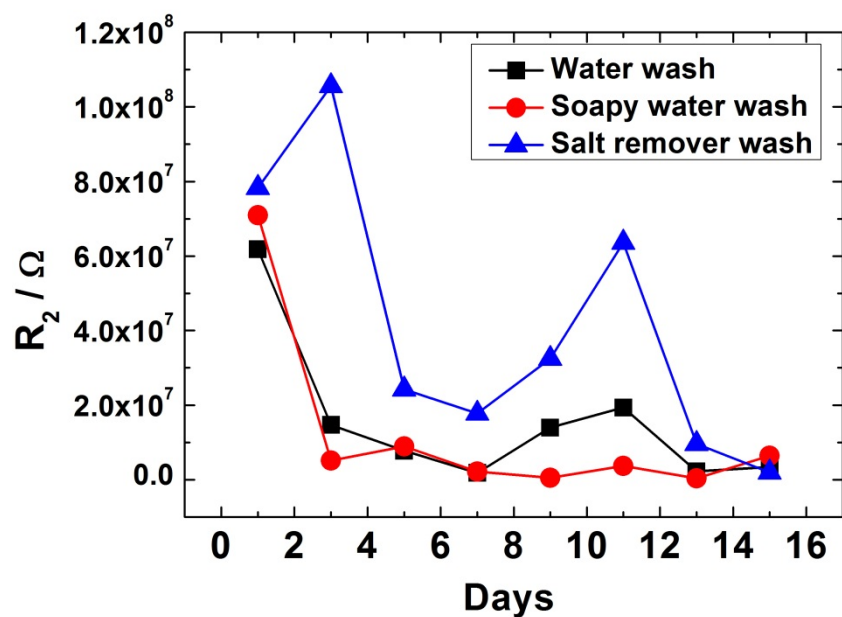


Figure 19. The relationship between charge transfer resistance (R_2) and the days from stainless steel coupons (SS304L) in a 30 wt.% $MgCl_2$ solution.

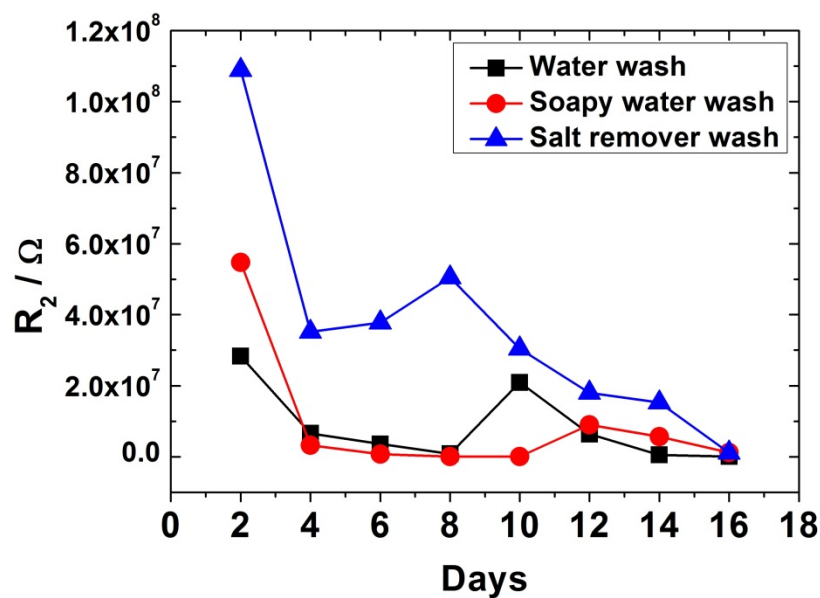


Figure 20. The relationship between charge transfer resistance (R_2) and the days from stainless steel coupons (SS304L) in a 0.1 wt.% $MgCl_2$ solution.

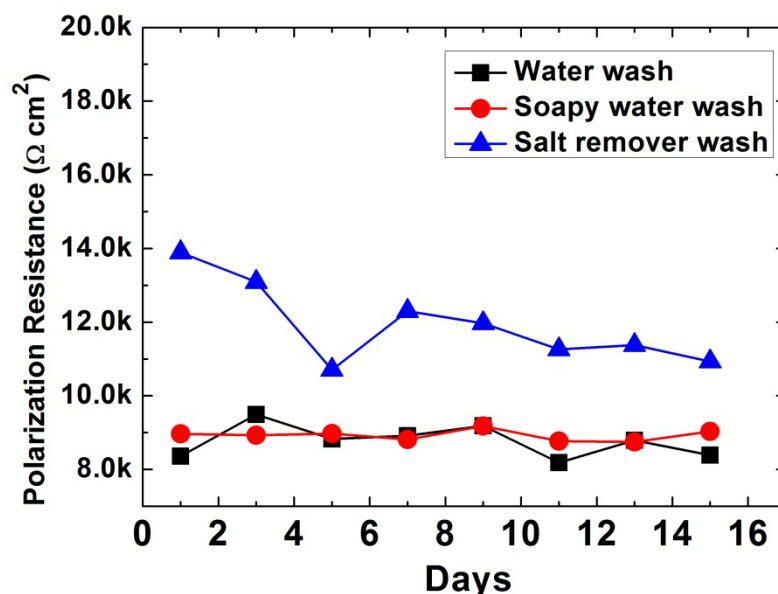


Figure 21. Temporal evolution of polarization resistance of stainless steel coupons (SS304L) in a 30 wt.% MgCl_2 solution.

In summary, from the wet-dry test, it can be concluded that the power-washing with salt remover *HoldTight* (to a less extent, soapy water) can significantly enhance the anti-corrosion property of carbon steel and stainless steel in 30% MgCl_2 solution. However, obvious improvement of anti-corrosion property can not be observed from the aluminum alloy.

3.4. MAS Assessing Metallic Corrosion under Deicer Environments

Corrosion of Metals As a Result of Cyclic Exposure to Diluted NaCl

Figure 22 shows that, after exposed in the diluted (2.3%) NaCl deicer environment, no sign of corrosion occurred on the sensor surfaces of 1100 Al or 314 SS, even in the absence of spray-on corrosion inhibitors. In contrast, in the absence of sprayed corrosion inhibitors, all nine probes of the 1008 CS sensor showed signs of serious corrosion. The two sprayed inhibitors apparently mitigated the deicer-induced corrosion of carbon steel, even though there were visible corrosion products formed on the sensor surfaces. For all three coated MAS sensors, their coatings all showed a certain degree of degradation (e.g., blistering) after the cyclic exposure to diluted NaCl.

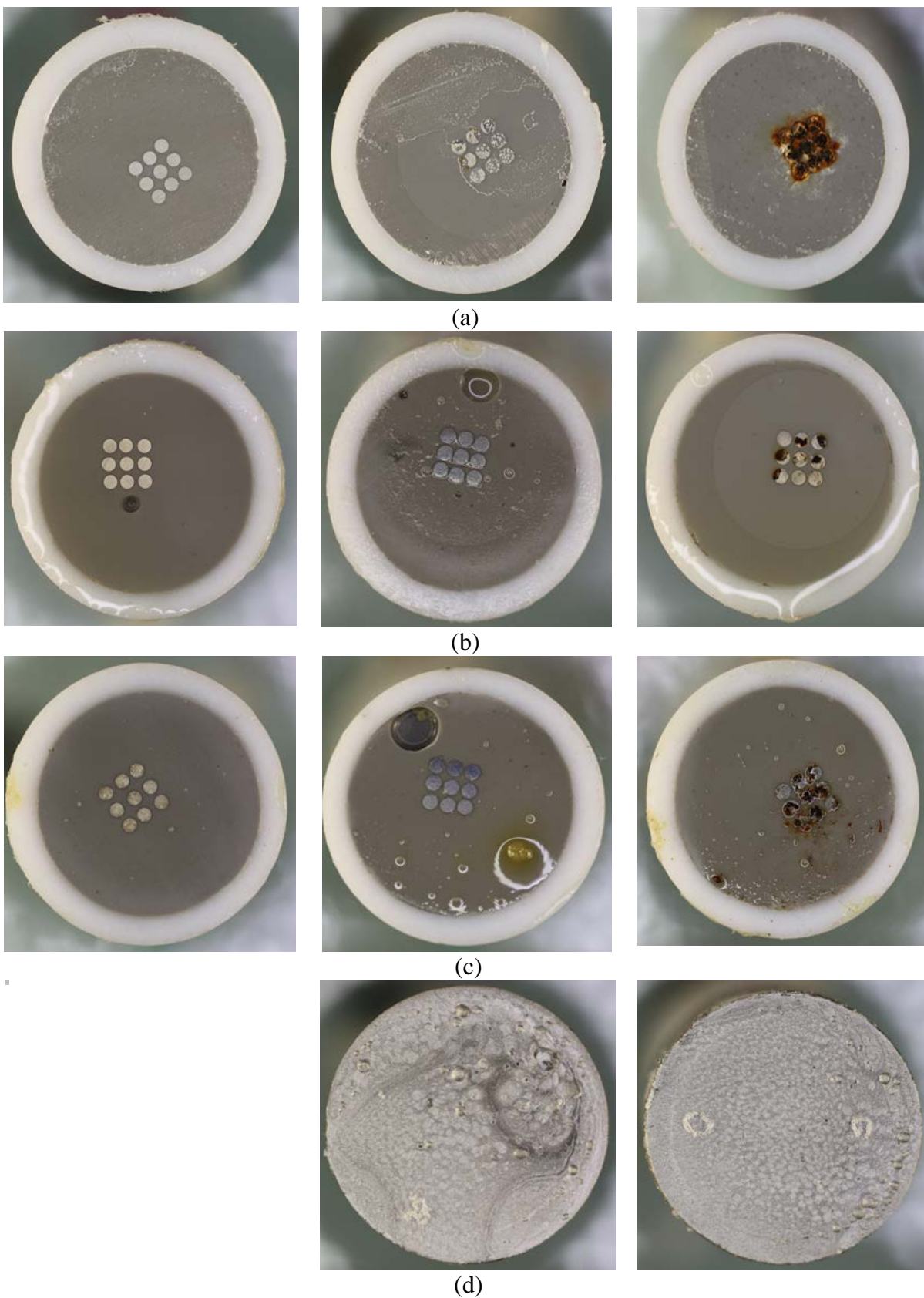


Figure 22. Sensor surface morphology after 8 cyclic exposure in 2.3% NaCl deicer

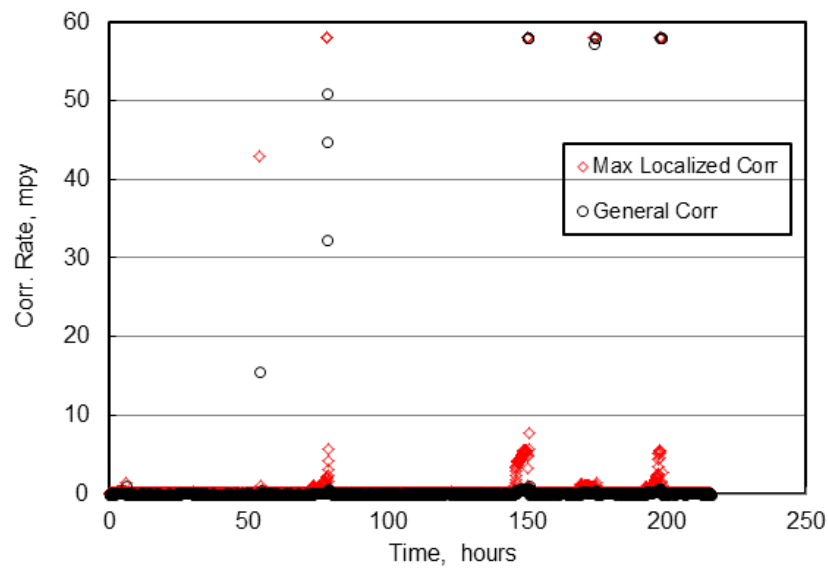
environment: (a) control group, (b) sensors spray-applied with inhibitor *Krown T40*, (c) sensors spray-applied with inhibitor *Rust Oleum*, and (d) sensors protected by coating *Rust Bullet*. Sensor material: Left: 1100 Al; Middle: 304 SS; Right: 1008 CS

For each type of metal, the MAS probes reported the temporal evolution of average and maximum localized corrosion rates (in milli-inches per year, *mpy*), which further provide quantitative insights about their corrosion during the cyclic exposure to 2.3% NaCl solutions. These data are plotted in Figure 23 to Figure 25, which indicated that for all the materials tested, their corrosion rates fluctuated with the time of cyclic exposure. Furthermore, both the average and localized corrosion rates increased abruptly in the beginning of humid stage and stayed relatively high until the end of the salt application stage. Once the dry stage began, the corrosion rates started to decrease to a very low level (almost negligible, even for the carbon steel sensor in the control group). This trend is especially significant for the maximum localized corrosion rate. This trend also holds true regardless of the metal type and the presence of protective film, thus highlighting the importance of *de-humidified storage of equipment wherever possible*.

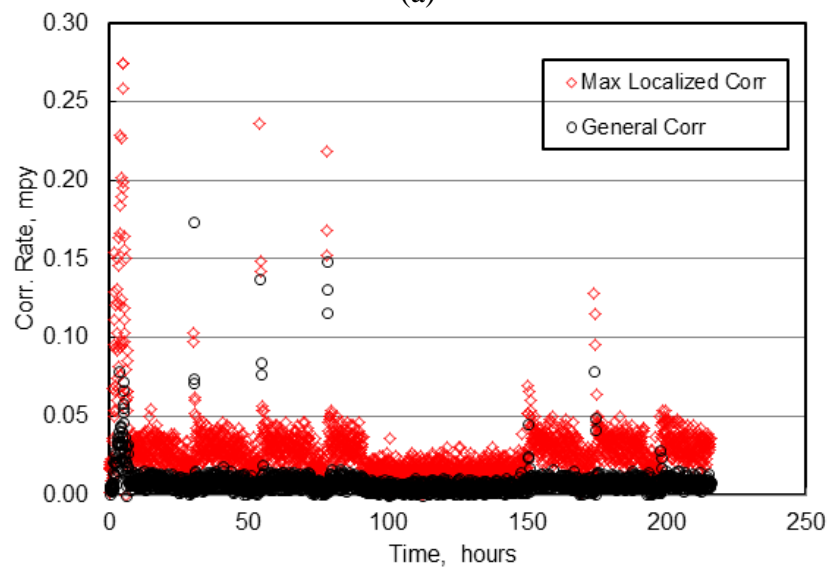
As shown in Figure 25(a), the 1008 CS sensor in the control group showed significantly high corrosion rates. The maximum localized corrosion rates in the early period of the humid stage were about 60 *mpy* and the average corrosion rates were more than 10 *mpy*. As shown in Figure 25(b), the maximum localized corrosion rate for the carbon steel sensor with inhibitor *Krown T40* during the humid stage was approximately 0.3 *mpy*, validating the benefits of periodically spraying such inhibitor for corrosion protection of carbon steel (as shown in Figure 22). As shown in Figure 25(c) and (d), the maximum localized corrosion rate for the carbon steel sensor with inhibitor *Rust Oleum* and coating *Rust Bullet* during the humid stage was approximately 0.25 *mpy* and 0.15 *mpy*, respectively.

Similarly, Figure 23 indicate that the application of *Krown T40*, *Rust Oleum* and *Rust Bullet* effectively reduced the maximum localized corrosion rate of the 1100 Al sensor from about 60 *mpy* to approximately 0.27 *mpy*, 0.28 *mpy*, and 0.16 *mpy*, respectively. Figure 24 indicates that the application of *Krown T40*, *Rust Oleum* and *Rust Bullet* effectively reduced the maximum localized corrosion rate of the 314 SS sensor from about 6.5 *mpy* to approximately 0.15 *mpy*, 0.24 *mpy*, and 0.12 *mpy*, respectively.

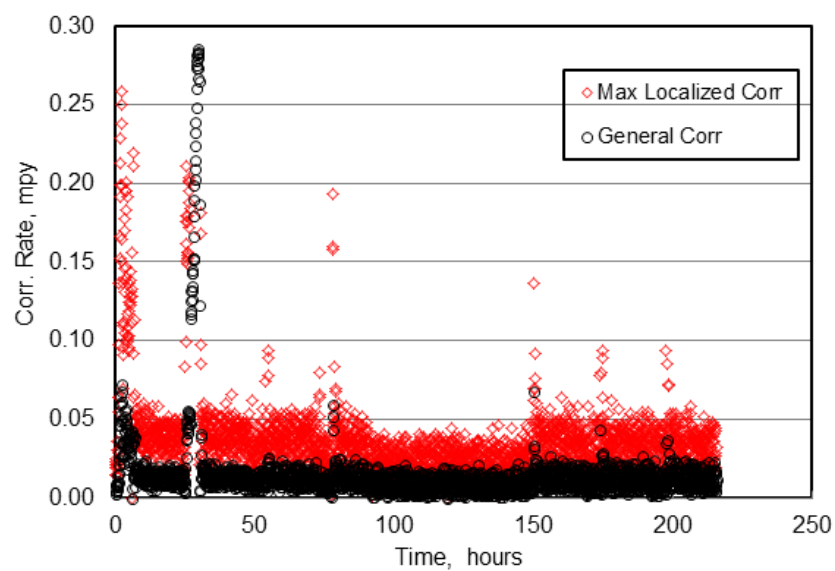
There were occurrences of localized corrosion for all three types of metals. However, for the 1100 Al and 314 SS sensors, the data showed a tendency of less localized corrosion over time, likely attributable to the self-passivation capability of these two metals. Relative to 1008 CS, the benefits of spray-on corrosion inhibitors or one-time coating were not as substantial for 1100 Al and 314 SS substrates.



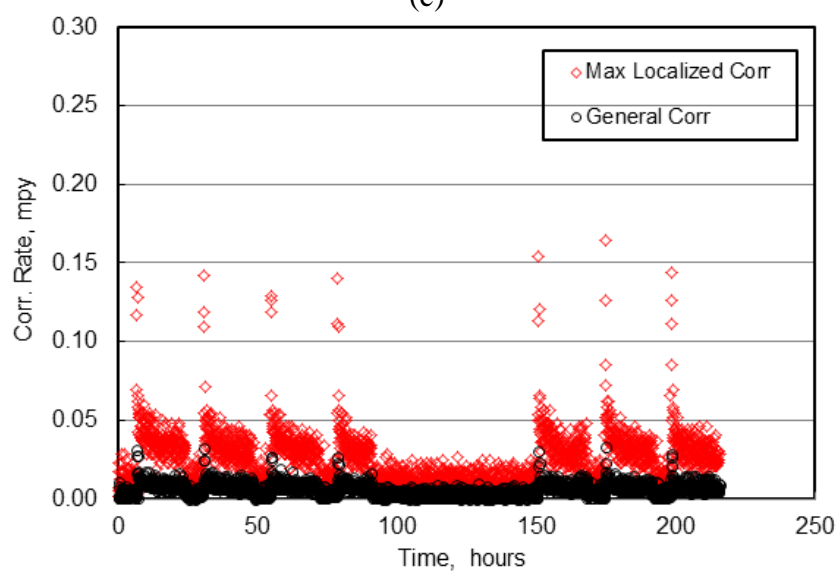
(a)



(b)

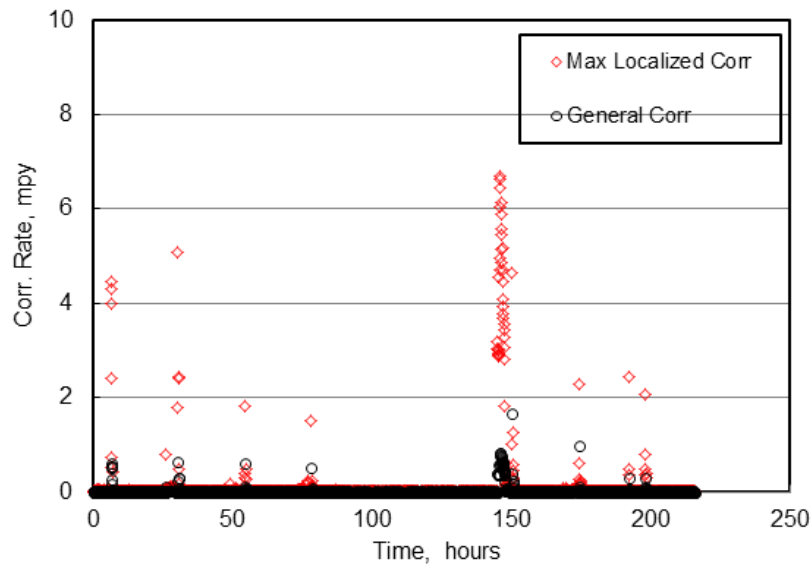


(c)

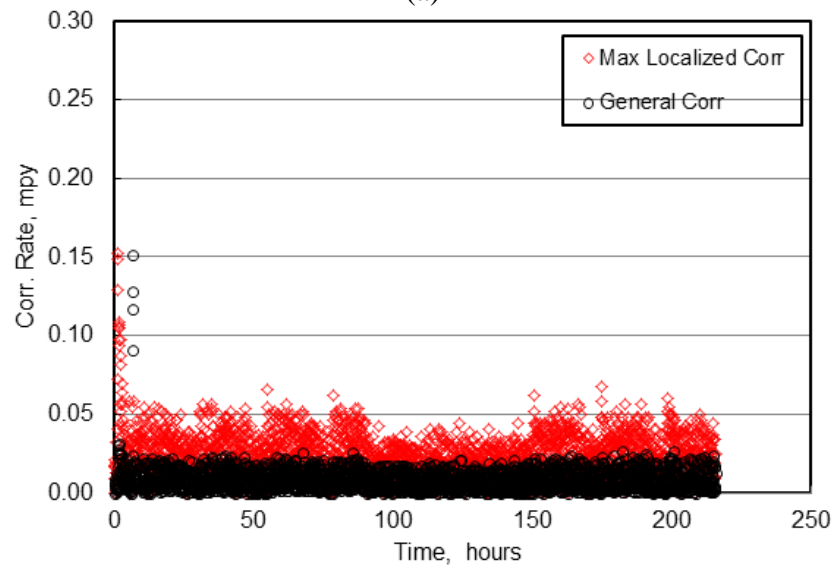


(d)

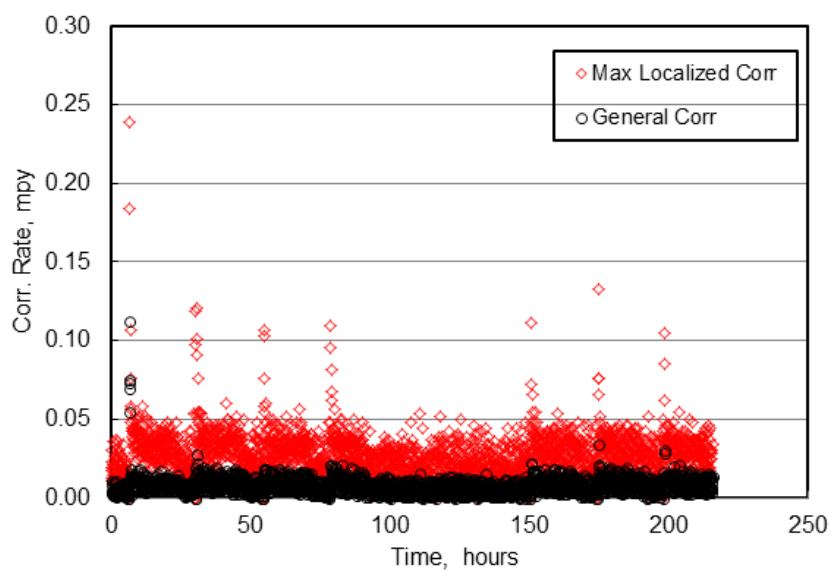
Figure 23. Corrosion rate of Al sensors within 2.3% NaCl deicer solution as function of exposure time. (a) control, (b) sensor spray-applied with inhibitor *Krown T40*, (c) sensor spray-applied with inhibitor *Rust Oleum*, and (d) sensor protected by coating *Rust Bullet*.



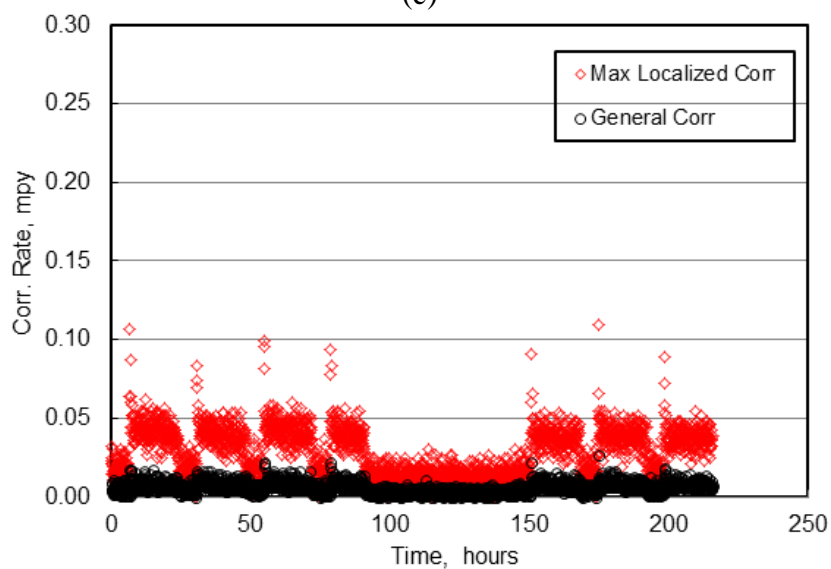
(a)



(b)

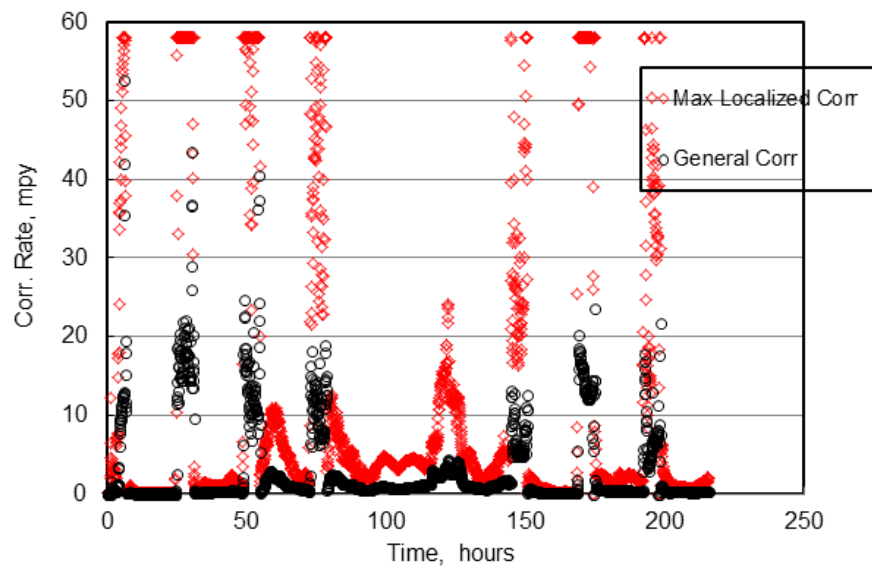


(c)

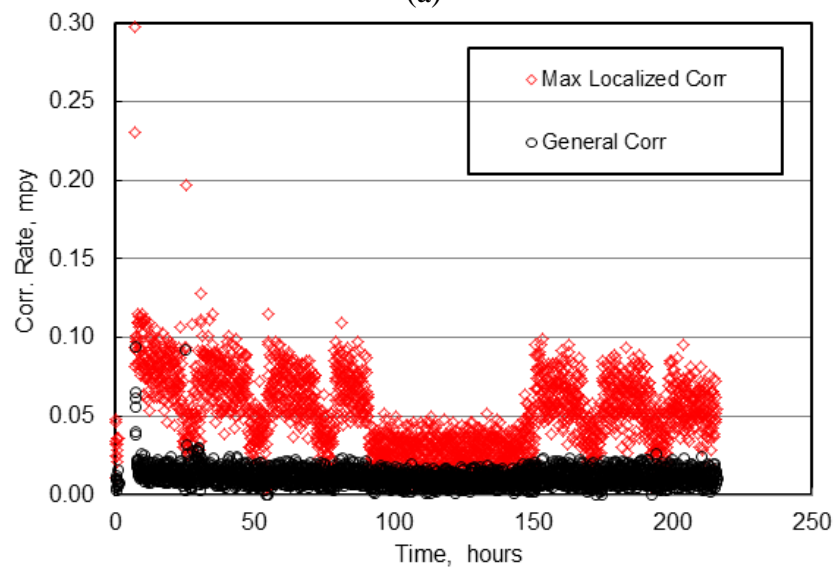


(d)

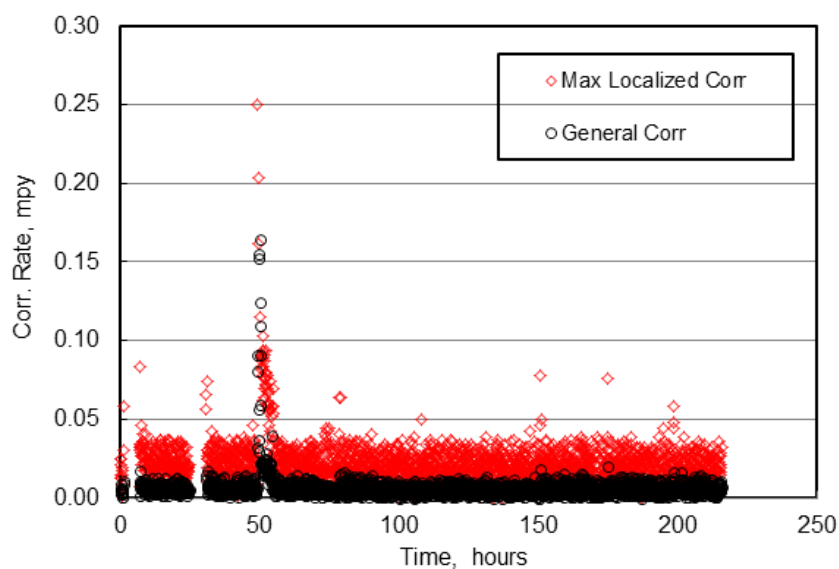
Figure 24. Corrosion rate of SS sensors within 2.3% NaCl deicer solution as function of exposure time. (a) control, (b) sensor spray-applied with inhibitor *Krown T40*, (c) sensor spray-applied with inhibitor *Rust Oleum*, and (d) sensor protected by coating *Rust Bullet*.



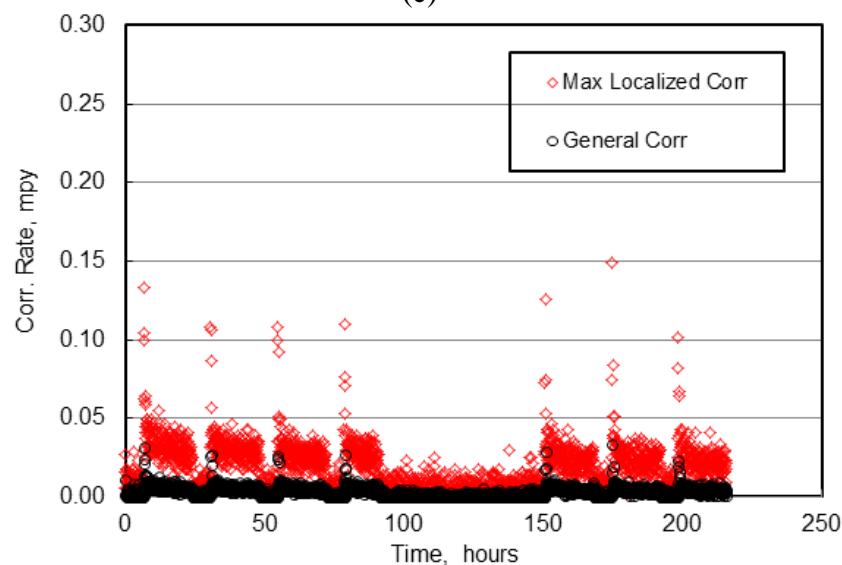
(a)



(b)



(c)



(d)

Figure 25. Corrosion rate of CS sensors within 2.3% NaCl deicer solution as function of exposure time. (a) control, (b) sensor spray-applied with inhibitor *Krown T40*, (c) sensor spray-applied with inhibitor *Rust Oleum*, and (d) sensor protected by coating *Rust Bullet*.

Corrosion of Metals As a Result of Cyclic Exposure to Diluted $MgCl_2$

Figure 26 shows that, after exposed in the diluted (3.0%) $MgCl_2$ deicer environment, no any corrosion sign occurred on the sensor surfaces of 1100 Al, even in the absence of spray-on corrosion inhibitors. In contrast, in the absence of sprayed corrosion inhibitors, all nine probes of the 1008 CS sensor showed signs of serious corrosion and even some probes of the 314 SS showed signs of corrosion. The two sprayed inhibitors apparently mitigated the deicer-induced corrosion of carbon steel, and there were no visible corrosion products

formed on the sensor surfaces. In other words, even though the cyclic exposure to diluted MgCl_2 poses more corrosion risk to 314 SS and 1008 CS than that to diluted NaCl, such risks are better mitigated by the spray-on corrosion inhibitors tested. For all three coated MAS sensors, their coatings all showed some degree of degradation (e.g., blistering) after the cyclic exposure to diluted MgCl_2 .



(a)



(b)



(c)



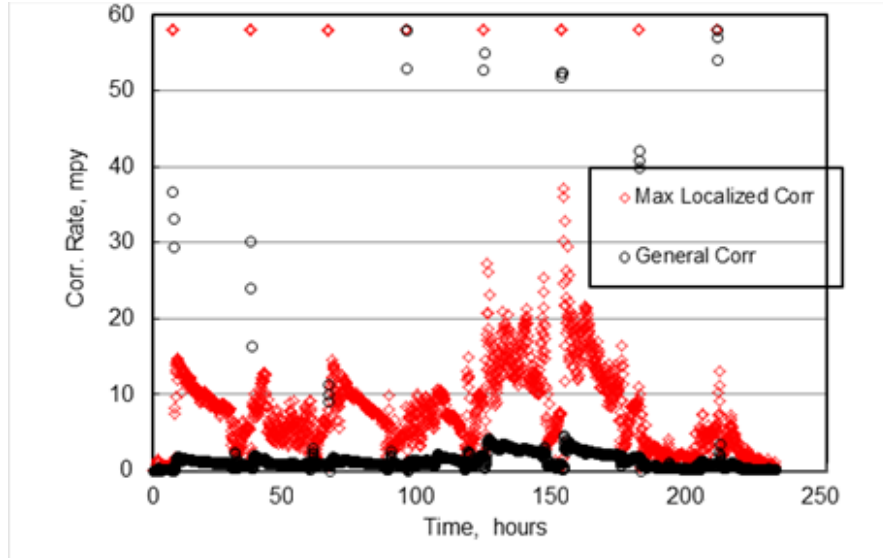
(d)

Figure 26. Sensor surface morphology after 8 cyclic exposure in 3.0% MgCl_2 deicer environment: (a) control group, (b) sensors spray-applied with inhibitor *Krown T40*, (c) sensors spray-applied with inhibitor *Rust Oleum*, and (d) sensors protected by coating *Rust Bullet*. Sensor material: Left: 1100 Al; Middle: 304 SS; Right: 1008 CS

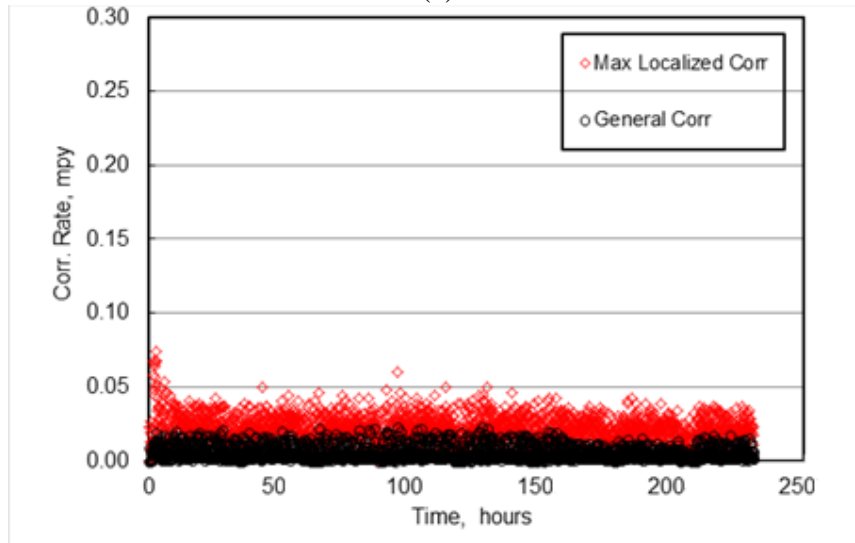
For each type of metal, the MAS probes reported the temporal evolution of average and maximum localized corrosion rates, which further provide quantitative insights about their corrosion during the cyclic exposure to 3.0% MgCl_2 solutions. These data are plotted in Figure 27 to Figure 29, which indicated that for all the materials tested, their corrosion rates fluctuated with the time of cyclic exposure. For the sensors in the control group (not protected by inhibitor or coating), their corrosion rates (Figure 27(a), Figure 28(a) and Figure 29(a)) reveal that all three materials cyclically exposed to diluted MgCl_2 experienced more severe corrosion, both maximum localized corrosion and general corrosion, relative to those exposed to diluted NaCl (Figure 23 to Figure 25(a)). An interesting finding is that after experienced rapid corrosion rate increase at the beginning of humid stage, the corrosion rate, both maximum localized and general corrosion rate, dropped slowly throughout the whole cycle, including all three stages. This differed significantly from the case in the NaCl deicer exposure, where the corrosion rate drops quickly at the beginning of each dry stage. It is mainly attributable to the lower deliquescence RH for MgCl_2 (35% RH), relative to that of NaCl (76% RH). Different from NaCl , the inherently hygroscopic nature of MgCl_2 crystals enable them to retain more moisture and remain as a corrosive solution at lower RH values observed during the dry stage. Again this highlights the importance of *de-humidified storage of equipment wherever possible*. Note that for equipment in the field service environments, the higher viscosity of MgCl_2 solution makes it more difficult to be removed from the metal surfaces than NaCl .

As shown in Figure 29(a), the 1008 CS sensor in the control group showed significantly high corrosion rates. The maximum localized corrosion rates in the early period of the humid stage were about 60 mpy and the average corrosion rates were more than 20 mpy. As shown in Figure 29(b), the maximum localized corrosion rate for the carbon steel sensor with inhibitor *Krown T40* during the humid stage was approximately 0.13 mpy, validating the benefits of periodically spraying such inhibitor for corrosion protection of carbon steel. As shown in Figure 29(c) and (d), the maximum localized corrosion rate for the carbon steel sensor with inhibitor *Rust Oleum* and coating *Rust Bullet* during the humid stage was approximately 0.27 mpy and 0.12 mpy, respectively.

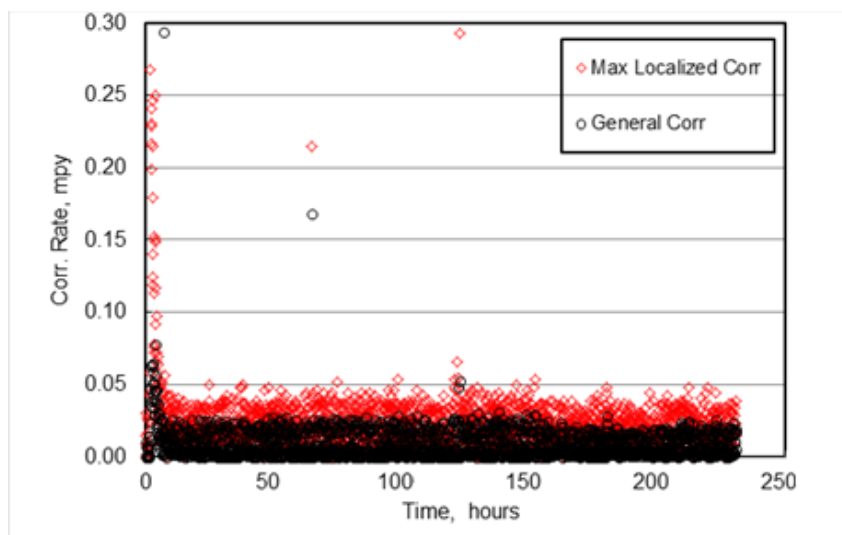
Similarly, Figure 27 indicate that the application of *Krown T40*, *Rust Oleum* and *Rust Bullet* effectively reduced the maximum localized corrosion rate of the 1100 Al sensor from about 60 mpy to approximately 0.08 mpy, 0.03 mpy, and 0.15 mpy, respectively. Figure 28 indicates that the application of *Krown T40*, *Rust Oleum* and *Rust Bullet* effectively reduced the maximum localized corrosion rate of the 314 SS sensor from about 28 mpy to approximately 0.05 mpy, 0.09 mpy, and 0.06 mpy, respectively.



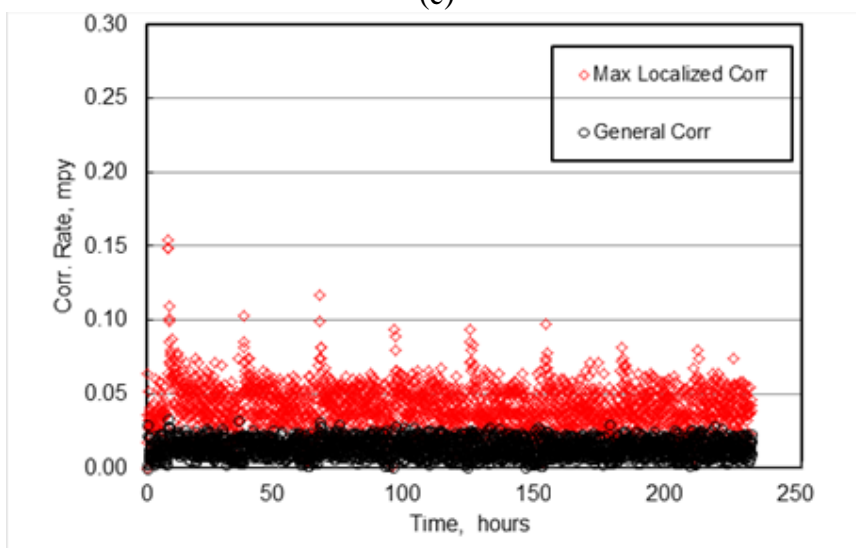
(a)



(b)

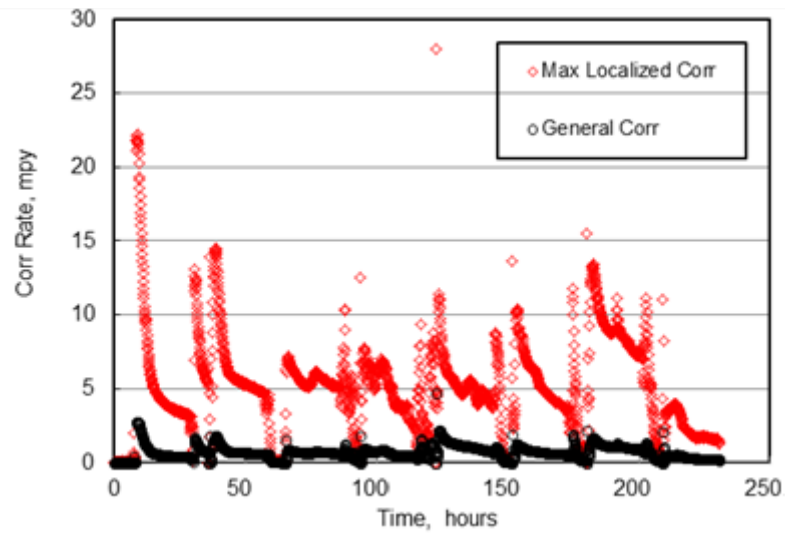


(c)

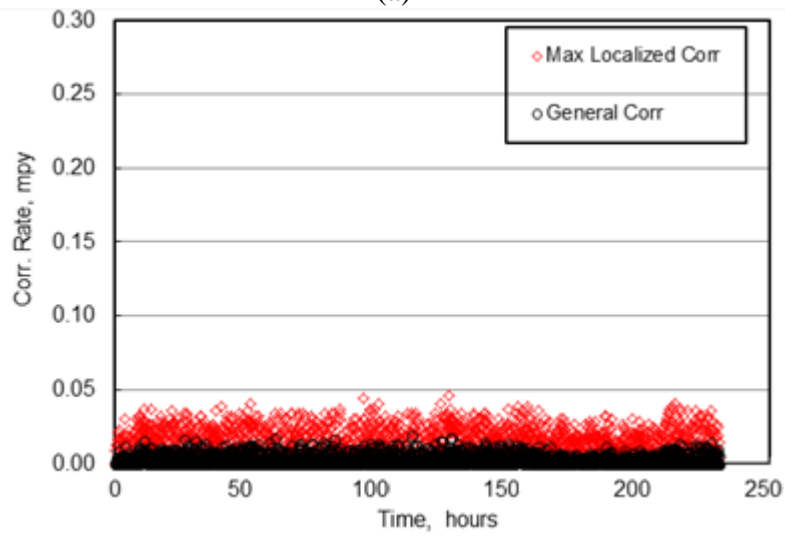


(d)

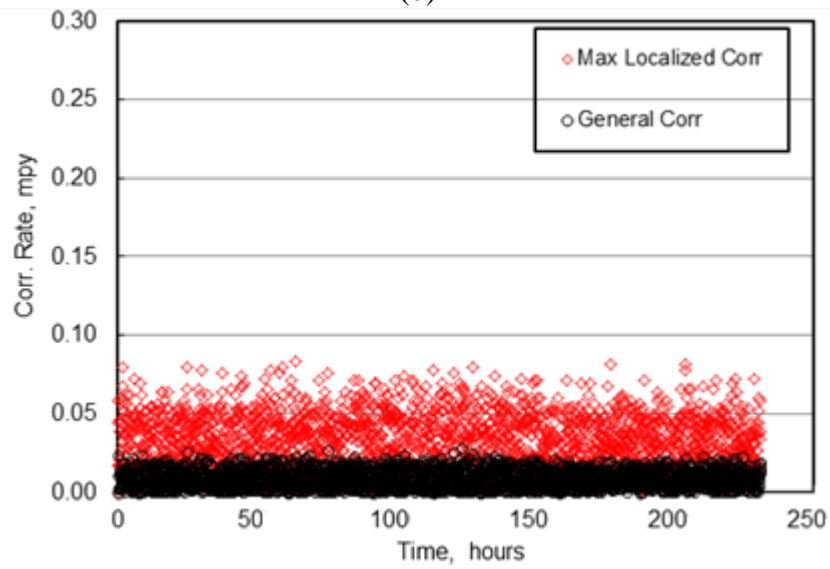
Figure 27. Corrosion rate of Al sensors within 3.0% MgCl_2 deicer solution as function of exposure time. (a) control, (b) sensor spray-applied with inhibitor *Krown T40*, (c) sensor spray-applied with inhibitor *Rust Oleum*, and (d) sensor protected by coating *Rust Bullet*.

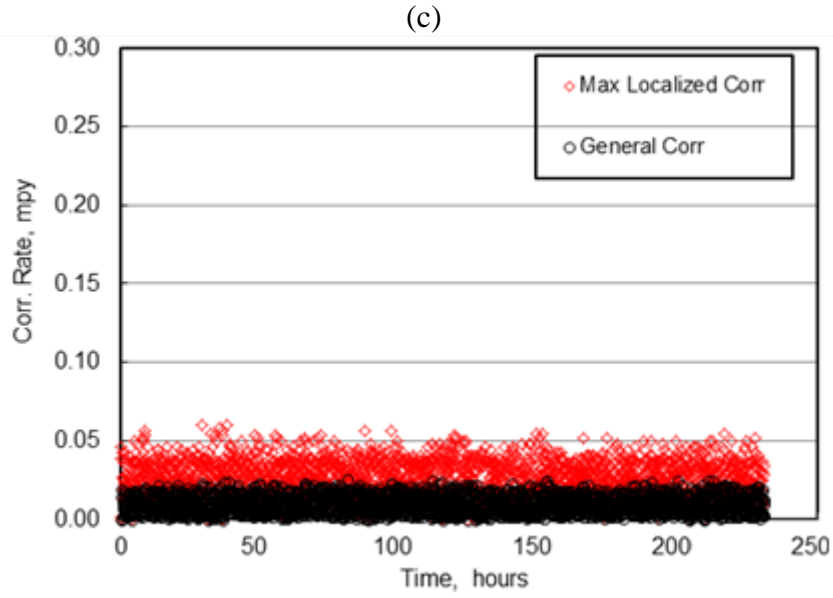


(a)



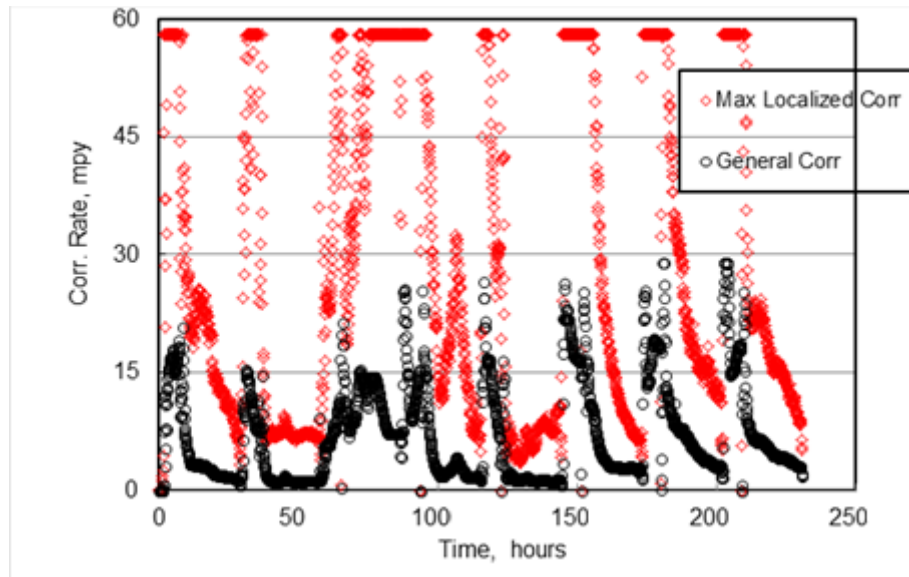
(b)



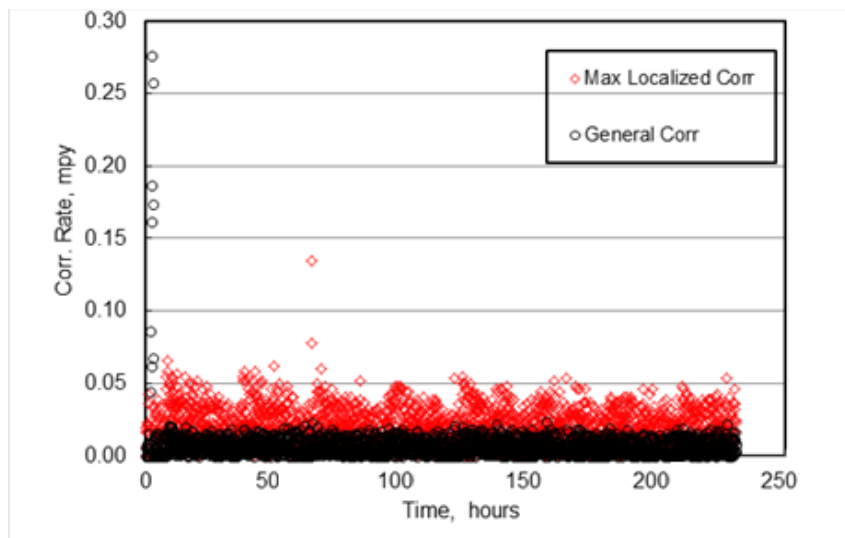


(d)

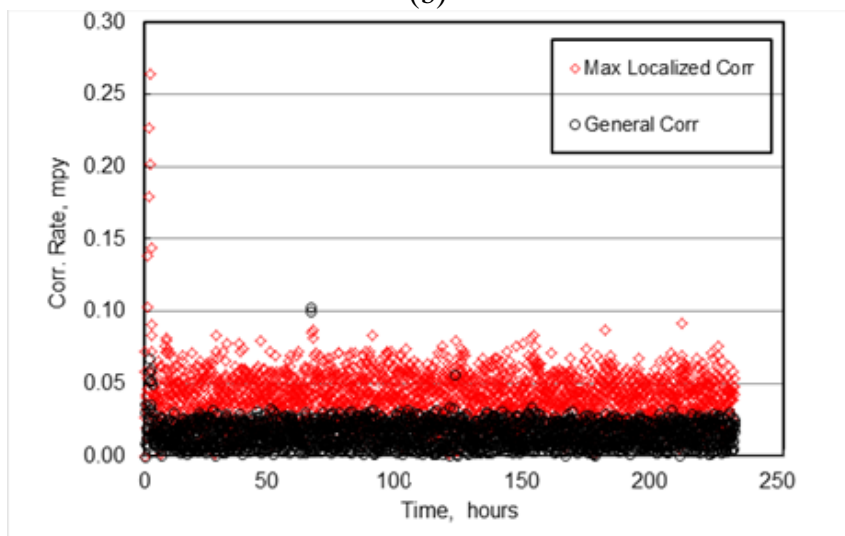
Figure 28. Corrosion rate of SS sensors within 3.0% MgCl_2 deicer solution as function of exposure time. (a) control, (b) sensor spray-applied with inhibitor *Krown T40*, (c) sensor spray-applied with inhibitor *Rust Oleum*, and (d) sensor protected by coating *Rust Bullet*.



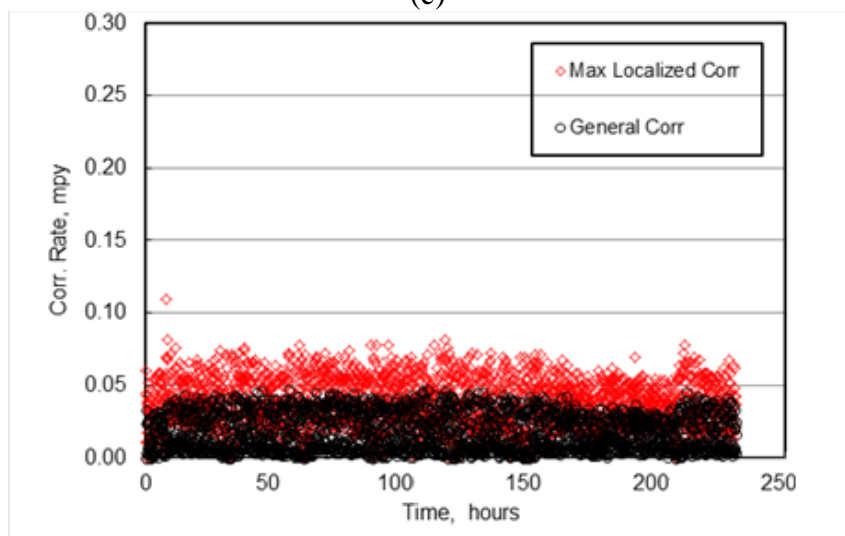
(a)



(b)



(c)

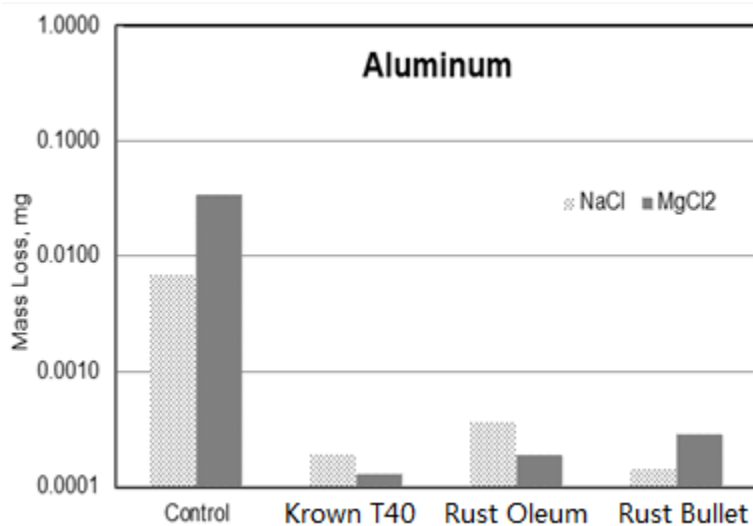


(d)

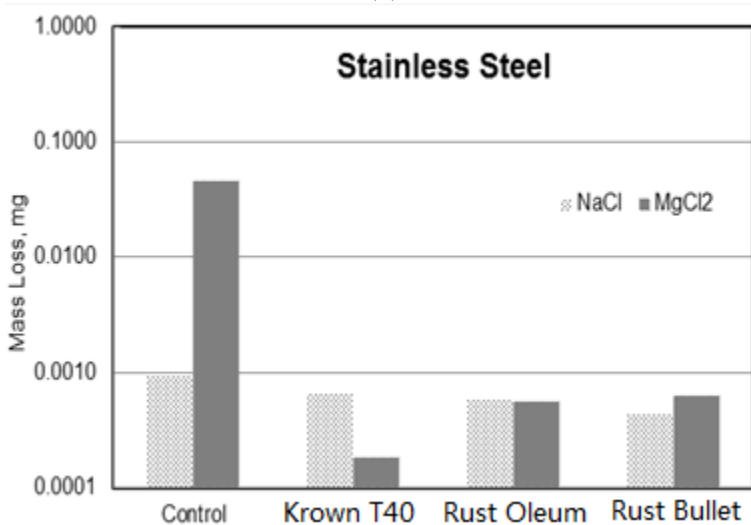
Figure 29. Corrosion rate of CS sensors within 3.0% MgCl_2 deicer solution as function of exposure time. (a) control, (b) sensor spray-applied with inhibitor *Krown T40*, (c) sensor spray-applied with inhibitor *Rust Oleum*, and (d) sensor protected by coating *Rust Bullet*.

Comparing MAS Corrosion Data in the Two Diluted Deicer Solutions

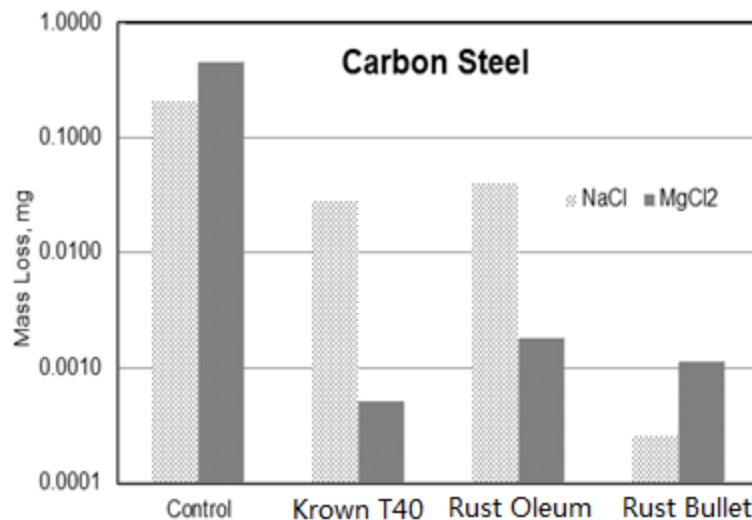
The total mass loss of electrodes in each individual sensor was calculated according to Faraday's law using the corrosion current data reported in the previous figures. Figure 30 shows the comparison for mass loss of CS, SS, and Al sensors in four groups under the NaCl and MgCl_2 deicer environments, respectively. These average corrosion rate results confirm the same trends discussed in the previous sections, i.e., the maximum and average corrosion current data from the MAS sensors.



(a)



(b)



(c)

Figure 30. Comparison of mass loss results in four groups under the NaCl and MgCl₂ deicer environments: (a) Al MAS; (b) SS MAS; (c) CS MAS.

EIS and Corrosion Morphology Scans of CS Panels after Cyclic Exposure

As detailed in this section, electrochemical impedance and 3D laser profilometer measurements were conducted for the CS plates in the similar cyclic exposure environment, and the results confirmed the findings obtained from the MAS measurements.

Figure 31 shows the Bode plots of CS panels cyclically exposed in 2.3% NaCl aqueous solution with or without the inhibitors applied respectively. The EIS measurements of each panel were conducted at the end of the immersion stage of 1st, 3rd, and 8th cycles, respectively. The results indicate that, without inhibitor application (the control panels), the impedance values were relative low, in the range of 1,000 ~1,400 ohms at the low frequency. There was a steady decrease in the low-frequency impedance values, as the CS panels were subjected to the cyclic deicer exposure. In contrast, the application of spray-on inhibitor (Krown T40 or Rust Oleum) considerably improved the impedance values measured from the CS panels. At the end of the 8th exposure cycle, the impedance was 3 or 2 orders of magnitude more for the panels with Krown T40 and Rust Oleum applied, respectively, relative to the control panels, confirming the great corrosion protection benefits offered by these inhibitors.

It is noteworthy that under the investigated conditions, **Krown T40** provided higher ultimate impedance (after 8th cycle) for the CS panels as well as quicker protection (after 1st cycle), relative to Rust Oleum. This is consistent with the EIS results for continuous immersion in 3% MgCl₂, reported earlier in Table 13. For the inhibitor-protected CS panels, there was generally a steady increase in the impedance values with the number of exposure cycles, implying that the inhibitors were not readily removed during the immersion conditions.

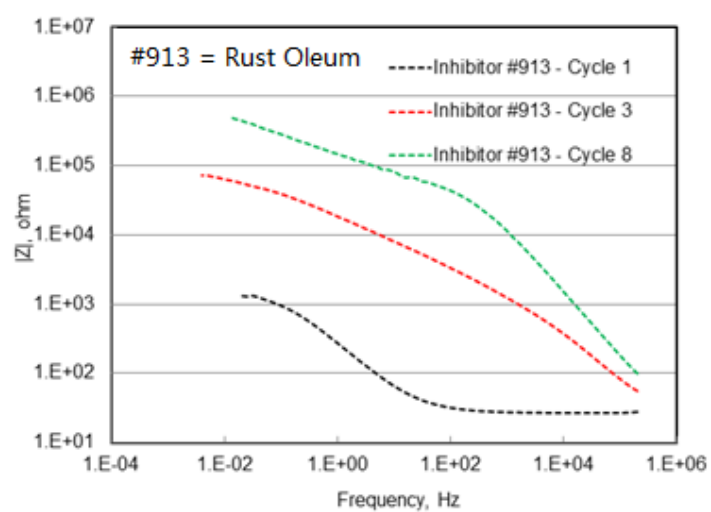
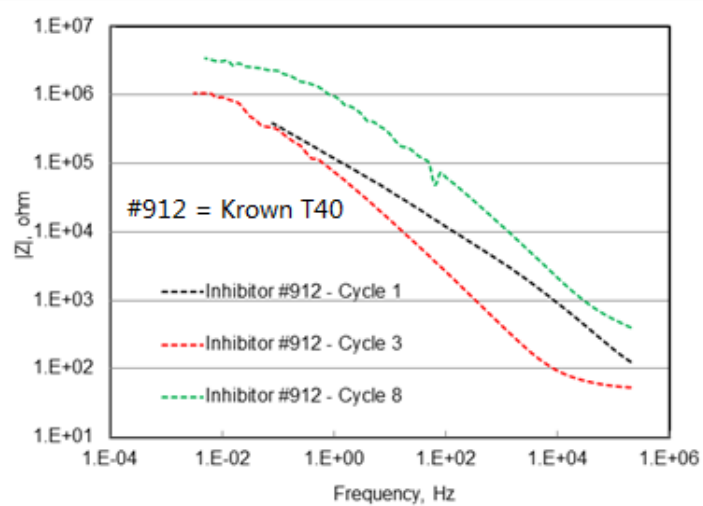
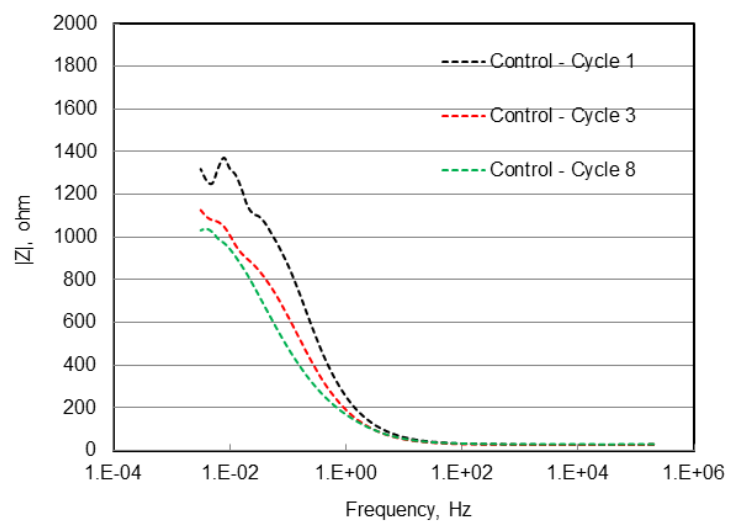
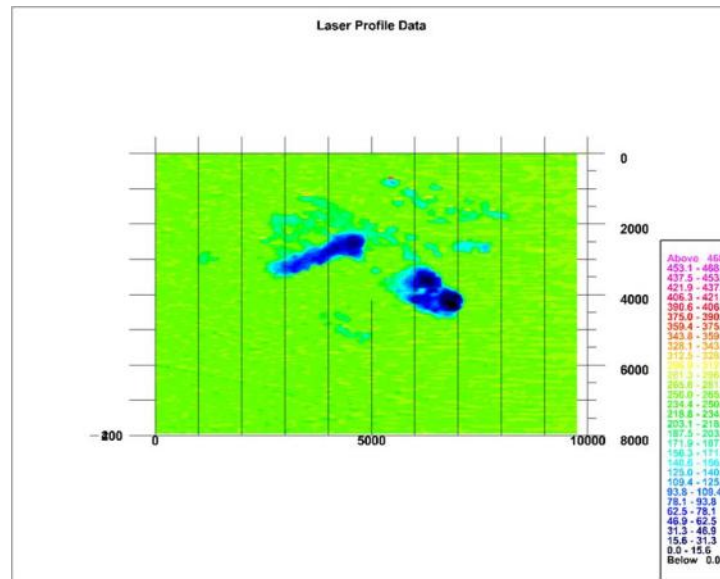
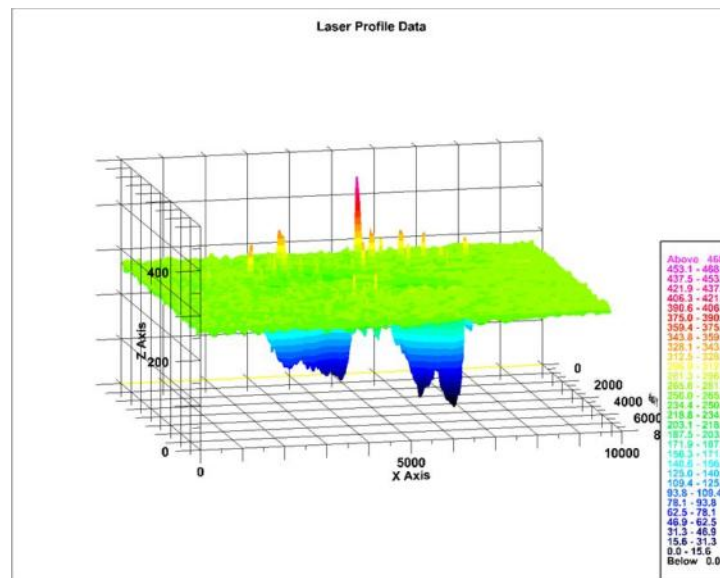


Figure 31. EIS (Bode) plots of CS panels cyclically exposed in 2.3% NaCl solution, with or without the spray-on corrosion inhibitors applied.

Figure 32 and Figure 33 shows the corrosion morphology profile of CS panels after 8 exposure cycles to 2.3% NaCl solution, with inhibitor Krown T40 and Rust Oleum periodically applied, respectively. There are two localized corrosion regions with approximately 250 μm depth of attack in the Krown-protected CS panel (Figure 32). In contrast, the Rust-Oleum-protected CS panel (Figure 33) featured many small localized corrosion holes with maximum depth at approximately 150 μm . In other words, the Krown inhibitor led to less average corrosion of the CS panel yet the panel's localized corrosion was a bit more severe than the panel protected by the Rust Oleum inhibitor. This is consistent with the MAS results reported earlier where the Krown-protected MAS exhibited a bit higher maximum localized corrosion rates.

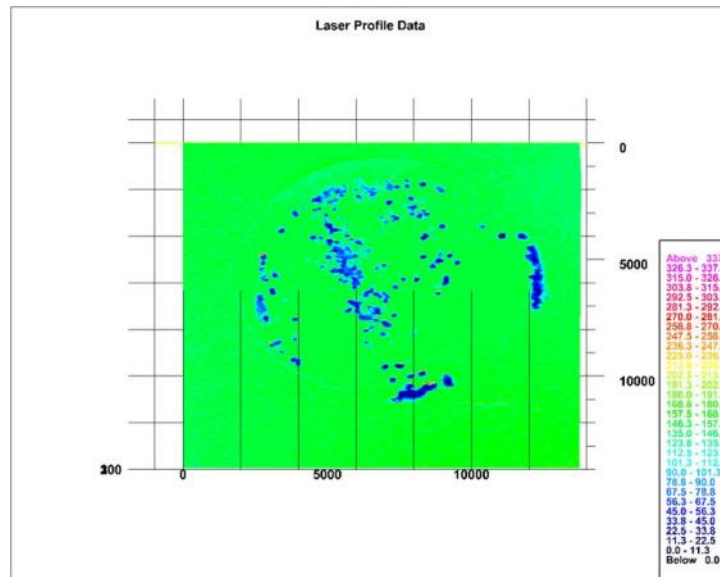


(a)

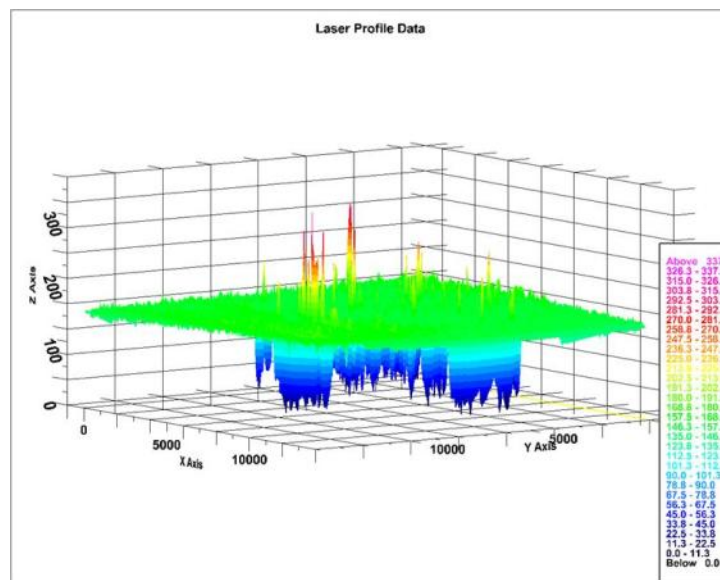


(b)

Figure 32. Corrosion morphology profile of a CS panel cyclic exposed in NaCl based deicer environment with inhibitor Krown T40 applied. (a) 2D and (b) 3D laser profilometer scans.



(a)



(b)

Figure 33. Corrosion morphology profile of a CS panel cyclic exposed in NaCl based deicer environment with inhibitor Rust Oleum applied. (a) 2D and (b) 3D laser profilometer scans.

Projecting the Corrosion Rates of Metals in the Field Environment

This section presents a preliminary effort to project the corrosion rates of metals in the field environment, based on the accelerated laboratory corrosion data of MAS exposed to the modified SAE J2334 tests described in the previous sections. To this end, one has to

recognize that the corrosion rate of the metals tested (CS, SS, and Al) will likely decrease over time and eventually stabilize, as shown in Figure 30. Figure 30 was established adopting the field exposure data of steel crevice coupons reported by the American Public Works Association Research Foundation (1970), with the upper set of data from coupons exposed to regular salt or inhibited salt (no significant difference between the two) and the lower set of data from coupons exposed to sand only. These data confirm that the exposure to NaCl-based deicers increased the corrosion rate of bare metal and this 1970 study concluded that “up to 50 percent of vehicle corrosion can be attributed to the action of deicing salt”. Figure 30 reveals that the corrosion rate of bare steel decreased exponentially over time, regardless of the deicer exposure. This lays the groundwork for our corrosion rate conversions described as follows.

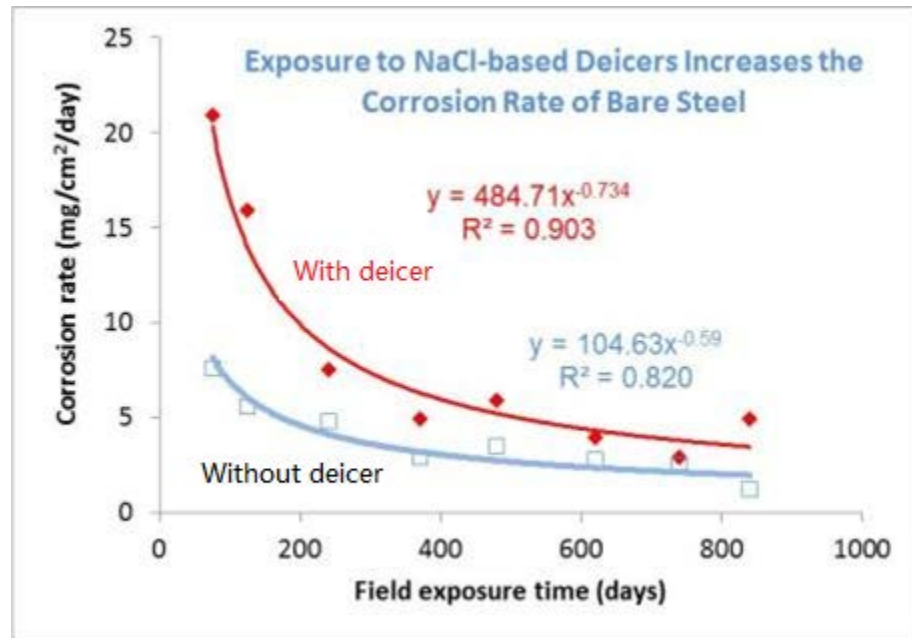


Figure 34. Corrosion rate of bare carbon steel as a function of field exposure time.

First of all, it has been found that 80 cycles of SAE J2334 accelerated laboratory test corresponded well with five years of outdoor, on-vehicle testing for steel (Wang et al., 2006). Considering that the corrosion rates of metals tend to be much higher in the early stage of exposure, we can reasonably assume that 8 cycles of SAE J2334 laboratory testing conducted by SwRI can be treated as approximately one year of outdoor testing, instead of 0.5 years. Table 15 shows the practical implications of the MAS data obtained from this study, by correlating them with outdoor, on-vehicle coupon exposure data reported by Stephens et al. (2006).

Table 15. Correlating the field exposure data with the accelerated laboratory testing of metallic corrosion by deicer exposure.

Material type	Deicer exposure	Test method	Conversion using worst-case scenario	Corrosion rate in the field
---------------	-----------------	-------------	--------------------------------------	-----------------------------

1008 CS	Various inhibited or non-inhibited NaCl and MgCl ₂ deicers	Outdoor, on-vehicle panels (gravimetric testing of corrosion rate)	Not applicable; actual data measured over 1 to 2 years of field exposure	8.26 mpy
SS				Not available; assumed to be 4.13 mpy (i.e., 50% of 1008 CS)
A356 cast Al				0.65 mpy
1008 CS	2.3% NaCl solution (3.0% MgCl ₂ solution)	SAE cycling + MAS (electrochemical testing of maximum localized corrosion rate)	60 mpy (60 mpy) divided by 7.26	8.26 mpy (converted)
CS w/ <i>Krown T40</i>			0.3 mpy (0.13 mpy) divided by 7.26	0.04 mpy (estimated), i.e., 99.5% protection
CS w/ <i>Rust Oleum</i>			0.25 mpy (0.27 mpy) divided by 7.26	0.03 mpy (estimated), i.e., 99.6% protection
CS w/ <i>Rust Bullet</i>			0.15 mpy (0.12 mpy) divided by 7.26	0.02 mpy (estimated), i.e., 99.8% protection
314 SS			6.5 mpy (28 mpy) divided by 6.78	4.13 mpy (converted)
SS w/ <i>Krown T40</i>			0.15 mpy (0.05 mpy) divided by 6.78	0.02 mpy (estimated), i.e., 99.5% protection
SS w/ <i>Rust Oleum</i>			0.24 mpy (0.09 mpy) divided by 6.78	0.04 mpy (estimated), i.e., 99.0% protection
SS w/ <i>Rust Bullet</i>			0.12 mpy (0.06 mpy) divided by 6.78	0.02 mpy (estimated), i.e., 99.5% protection
1100 Al			60 mpy (60 mpy) divided by 92.3	0.65 mpy (converted)
Al w/ <i>Krown T40</i>			0.27 mpy (0.08 mpy) divided by 92.3	0.003 mpy (converted), i.e., 99.5% protection
Al w/ <i>Rust Oleum</i>			0.28 mpy (0.03 mpy) divided by 92.3	0.003 mpy (converted), i.e., 99.5% protection
Al w/ <i>Rust Bullet</i>			0.16 mpy (0.15 mpy) divided by 92.3	0.002 mpy (converted), i.e., 99.7% protection

To estimate the appropriate frequency of applying the spray-on corrosion inhibitors, one can rely on the conservative conversion of 80 SAE test cycles to 5 years in the field environment. In other words, if one assumes the corrosion inhibitor is sprayed on the metal substrate per each SAE cycle, then the practical implication is that it should be sprayed on the exposed metallic components of DOT equipment/vehicles $80/5 = 19 \text{ times per year}$.

Arguably, the spraying of corrosion inhibitors would achieve the best efficiency in providing corrosion protection if it is applied more frequently during and immediately after the winter season than other times of the year and if it is applied immediately after the equipment is washed clean and dried.

As for the protective coating, it provided excellent protection of the metallic substrates during the first 8 SAE test cycles (equivalent of one year in the field environment) yet showed a certain degree of coating blistering after such cycling. Applying the protective coating every year would require labor-intensive and costly removal of the old coating and thus deemed impractical. Instead, additional research should be conducted to explore methods to minimize the risk of premature failure of the Rust Bullet coating (e.g., blistering and delamination). One potential approach to achieving improved performance of the coating is to admix small dosages of nano-sized materials into the select anti-corrosion coating, while reducing the dry film thickness (DFT) of the coating. Our research has demonstrated that the incorporation of nano-Fe₂O₃, nano-halloysite clay, nanosilica, or nano-Zn [31] into a solvent-based epoxy coating at 1% by mass of epoxy reduced the corrosion rate of bare carbon steel by 11 to 910 times, over a 28-day continuous immersion in 3% NaCl solution. The nano-modification by nanosilica also considerably improved the nano-mechanical properties of the coating, e.g., nano-Young's modulus. Other studies also reported the benefits of nano-modification of epoxy (and other coatings), in terms of improved fracture toughness, impact strength, storage modulus and Young's modulus. Well-dispersed nanoparticles are anticipated to enhance the integrity and durability of coatings, by filling cavities, bridging or deflecting cracks, preventing coating disaggregation during curing, reducing total free volume, increasing the cross-linking density, and improving barrier properties.

The following conclusions can be drawn based on the MAS testing results:

- 1) MAS sensor is an effective tool to *in situ* characterize corrosion of Al, SS, and SS materials in cyclic exposure environments, in the presence of corrosive deicer agents.
- 2) For all three materials in both MgCl₂ and NaCl exposure environments, the most severe corrosion occurred at the beginning of humid stage. Therefore, reducing the duration of wet exposure will effectively decrease material corrosion, especially localized corrosion. Wherever possible, agencies should consider *de-humidified storage of their equipment and vehicles*.
- 3) Even though the cyclic exposure to diluted MgCl₂ poses more corrosion risk to 314 SS and 1008 CS than that to diluted NaCl, such risks are better mitigated by the spray-on corrosion inhibitors tested.
- 4) Periodically spraying a corrosion inhibitor (*Krown T40*, 19 times per year) would effectively protect the aluminum, stainless steel, and carbon steel components on DOT equipment from corrosion related to NaCl or MgCl₂ deicers, by reducing their corrosion rate by at least 99%. Similarly, a one-time application of protective coating (*Rust Bullet*) reduced their corrosion rate by at least 99.5%, but additional research is needed to improve the integrity and durability of such coating over the years of field exposure.

3. 5. Findings from the Site Visit

WSDOT has been actively involved in extensive corrosion research and development projects as it has recognized the need to protect its equipment asset from deicer corrosion (e.g., Figure 31 and Figure 32). WSDOT has made substantial progress towards effective corrosion prevention methodologies and has been very proactive with various corrosion mitigation approaches such as appropriate deicer and corrosion inhibitor selection, equipment modification techniques, and regular maintenance schedules.

At WSDOT, modifications throughout snow and ice control equipment are implemented to mitigate the harmful effects of corrosion. These include: use of high-quality weather-proof terminations (e.g., buss-style connectors and compression fittings) in equipment specifications, elimination of junction boxes wherever possible, relocation of junction boxes to inside the cab off the floor, and use of sealed brake canisters and sealed protective boxes surrounding hydraulic components and batteries (as shown in Figure 33 to Figure 39). Electrical corrosion is a significant problem on snow and ice control equipment. WSDOT has implemented the use of high-quality weather-proof terminations and compression fittings in addition to shrink wrapping susceptible electrical wiring components.

WSDOT indicated the advantages of preventative maintenance (PM) program, such as: consistent washing after application, regular rinsing and localized cleaning, eliminating areas that solids and liquids may accumulate, using high-quality primers and topcoats in equipment specifications, using composite materials less susceptible to corrosion, and protecting new and replacement components prior to installation with wraps, covers, or shields. The benefits include the elimination of certain types of corrosion, savings in repair parts and labor costs, reduction in equipment down time, extended service life, and better planning [39].

Practices of reactive maintenance can be beneficial as well, such as neutralizing the existing corrosion (e.g., via abrasive blasting and steam cleaning and/or chloride neutralizer spray) and cleaning the area or material that was corroded [39]. For instance, some products tested and used by WSDOT to mitigate deicer corrosion to equipment include: Martin Senour DTM 5225 3.5 VOC gray epoxy primer, Martin Senour PRISM 3.5 VOC gloss black acrylic urethane, Martin Senour 6599 cleanable hardener, Neutro-Wash™ salt and chloride neutralizer (RHOMAR industries), Noco® battery cleaner and acid detector, and Densyl tape (Denso North America Inc.).

To define the significance of the deicer corrosion to equipment problem, various deicer usage and equipment asset data are provided in Table 16 to Table 20 as well as in Figure 40. WSDOT started tracking corrosion costs in 2008. For the entire WSDOT fleet, the corrosion-related repair costs and PM costs averaged 4.3% and 12.9% of the all repair costs (excluding PM costs), respectively. For the WSDOT snowplows, the corrosion-related repair costs and PM costs averaged 9.3% and 10.1% of the all repair costs (excluding PM costs), respectively.

In order to achieve the WSDOT recommended standard 12-year service life, certain components are replaced on a regular basis. Specifically, WSDOT stated that radiators on

trucks are replaced every two years due to corrosion and oil pans are replaced with more expensive zinc oil pans.



Figure 35. Side discharge salt spreader.



Figure 36. Side discharge salt spreader showing extensive corrosion.



Figure 37. Hydraulic components protected from corrosion using modified sealed protective cover.



Figure 38. Hydraulic components showing little to no corrosion due to sealed protective cover.



Figure 39. Protective cover for battery.



Figure 40. Modified protective cover for battery to reduce harmful effects of corrosion.



Figure 41. Rubber caps on battery terminals used to mitigate effects of corrosion.



Figure 42. New aluminum fuel tanks.

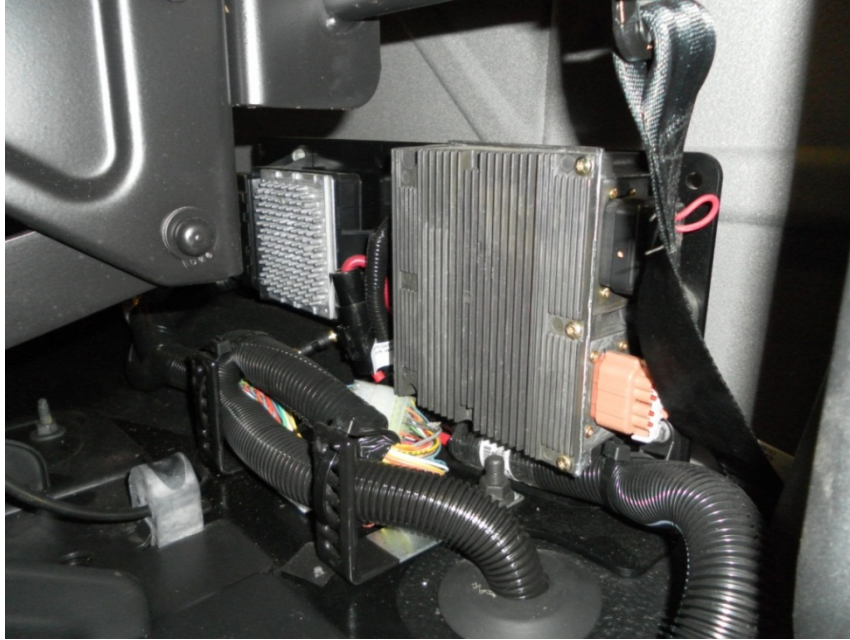


Figure 43. Modified electrical junction boxes are mounted inside the cab off the floor.

Table 16. Current equipment asset by WSDOT (top) and amount of chloride applied for deicing by WSDOT (bottom).

Asphalt Equipment	52	\$1,450,784.29
Attachments; Motor Grader, Front End Loader, and Excavators	46	\$295,537.96
Cranes and Shovels	31	\$1,874,997.67
Dump / Plow / Sander Trucks	503	\$41,638,767.69
Earth Drilling Equipment	26	\$2,227,967.65
Field Engineering Equipment	266	\$1,514,242.29
Front End Loaders	211	\$11,728,791.05
Fuel System Infrastructure	136	\$5,417,349.59
Incident Response Vehicles	87	\$1,205,104.75
Light Cargo Carrying Vans	153	\$1,871,617.64
Light Vehicles with Special Bodies or Equipment	333	\$8,125,870.29
Man-Lift and Digger / Derrick Trucks	109	\$9,406,976.10
Materials Laboratory Equipment	289	\$2,717,732.69
Motor Graders	35	\$2,550,220.75
OTEF Shop Equipment	241	\$1,373,706.69
Other Non-Self-Propelled Equipment	725	\$6,996,656.19
Other Self-Propelled Equipment	173	\$3,606,628.78
Passenger Carrying Vehicles	523	\$4,690,442.79
Photogrammetry Equipment	4	\$24,846.23
Pickup Trucks	1,154	\$13,275,541.69
Power Generation Equipment	157	\$1,475,520.74
Reproduction Equipment	19	\$54,712.38
Rollers	33	\$913,545.15
Self-Propelled (Riding) Mowers and Tractors	94	\$2,096,132.24
Snow Blowers	20	\$2,354,231.44
Snow Removal Attachments; Dump / Plow / Sander Trucks	544	\$5,883,086.09
Sweepers	66	\$3,944,636.93
Tractor Attachments	104	\$985,004.21
Trailers	265	\$4,225,712.61
Trucks Greater than 15,000 GVW; with Special Bodies	285	\$20,376,164.72
Wireless Communications Infrastructure Equipment	576	\$4,039,193.97
Wireless Communications User Equipment	27	\$216,908.82
Grand Total	7,287	\$168,558,632.08

Yearly Comparison of Tons of Chloride Applied for Deicing

	Fiscal Year 2007	Fiscal Year 2008	Fiscal Year 2009	Fiscal Year 2010	Fiscal Year 2011	Fiscal Year 2012
Northwest Region						
Area 1	1,734	1,733	1,728	826	1,517	1,457
Area 2	1,349	1,337	2,188	267	1,029	1,558
Area 3	1,152	1,009	2,812	503	1,546	1,980
Area 4	1,898	1,004	2,227	625	882	1,311
Area 5	1,880	1,543	3,764	587	3,323	3,092
Total	8,013	6,626	12,719	2,808	8,297	9,398
North Central Region						
Area 1	6,094	6,106	4,824	7,866	10,123	9,472
Stevens Pass	2,216	2,321	2,110	2,420	7,755	2,185
Area 2	3,497	4,615	3,129	3,280	6,656	4,592
Area 3	3,347	5,172	3,171	3,397	5,687	5,129
Total	12,938	15,893	11,124	14,543	22,466	19,193
Olympic Region						
Area 1	1,317	1,397	1,129	537	2,834	2,206
Area 2	1,350	1,749	2,485	338	2,373	2,089
Area 3	1,951	2,362	2,247	893	2,629	2,272
Area 4	1,015	1,133	1,931	366	1,488	1,395
Total	5,633	6,641	7,792	2,134	9,324	7,962
Southwest Region						
Area 1	1,307	1,300	2,612	856	1,890	1,326
Area 2	4,681	4,598	5,262	5,104	5,425	5,630
White Pass	2,852	3,224	2,224	880	2,960	3,035
Area 3	715	1,272	1,568	305	479	827
Area 4	2,050	3,093	3,159	2,314	2,739	2,468
Total	8,753	10,263	12,601	8,579	10,533	10,251
South Central Region						
Area 1	14,651	16,646	11,115	15,133	15,903	15,459
Hyak Pass	7,043	7,444	5,911	3,807	6,348	6,900
Area 2	2,775	4,751	2,619	3,212	5,251	4,221
Area 3	1,996	3,362	2,116	3,021	4,751	3,816
Area 4	1,595	2,606	1,941	1,731	2,607	2,010
Total	21,017	27,365	17,791	23,097	28,512	25,506
Eastern Region						
Area 1	4,592	9,319	6,545	4,943	6,952	5,676
Area 2	3,539	4,203	2,009	2,660	5,629	3,908
Area 3	3,185	6,389	5,720	5,580	5,071	2,577
Area 4	2,647	4,543	3,280	3,699	6,171	4,915
Total	13,963	24,454	17,554	16,882	23,823	17,076
GRAND TOTAL	70,317	91,242	79,581	68,043	102,955	89,386

Years 2007-2009 were supplied by PDA and AVL Data. Years 2010 - 2012 were from Data Mart

Table 17. Total repair costs of all WSDOT equipment.

All Repair Costs	2008	2009	2010	2011
Accessories (Electrical Accessories, Horns & Reverse Alarms, PTO, Winch, Towing Equip, Power Generation, Etc.)	\$515,186	\$479,345	\$621,084	\$569,950
Body	\$1,687,092	\$1,936,580	\$2,496,469	\$2,231,980
Bulk Fuel Dispensing System	\$348,011	\$455,219	\$343,790	\$326,434
Bulk Product Systems	\$63,449	\$55,291	\$74,849	\$67,969
Cab, Climate Control, Instrumentation	\$740,880	\$872,140	\$730,543	\$782,049
Chassis, Axles, Brakes, Frame, Steering, Suspension, Tires & Wheels	\$2,079,692	\$2,178,877	\$1,994,655	\$2,261,767
Complete Unit	\$1,565,742	\$954,761	\$625,602	\$829,096
Drive Train (Drive Axles, Clutch, Drive Shafts, Transfer Case, Transmission)	\$504,327	\$614,390	\$521,174	\$549,068
Electrical (Charging, Cranking, Ignition, Lighting)	\$1,371,092	\$997,589	\$1,123,508	\$1,121,578
Engine (Air Intake, Cooling, Exhaust, Fuel, Power Plant)	\$1,232,938	\$1,387,227	\$1,381,128	\$1,590,922
Equipment Dependent Attachments (Plows, Blades, Buckets, Hydraulics, Etc.)	\$3,375,186	\$3,671,945	\$3,305,515	\$3,935,673
Heating & Refrigeration	\$5,868	\$4,102	\$4,908	\$8,903
Obsolete	--	\$280	\$80,520	\$45,770
Preventative Maintenance Service (All Levels)	\$1,835,026	\$1,887,611	\$1,789,308	\$1,839,118
Wireless Communication	\$457,023	\$578,122	\$664,364	\$611,348
Grand Total	\$15,781,512	\$16,073,479	\$15,757,417	\$16,771,625

Table 18. Total repair costs of all WSDOT snowplows.

All Repair Costs	2008	2009	2010	2011
Accessories (Electrical Accessories, Horns & Reverse Alarms, PTO, Winch, Towing Equip, Power Generation, Etc.)	\$46,935	\$64,156	\$98,521	\$50,728
Body	\$1,599,025	\$1,432,672	\$2,041,939	\$1,522,590
Bulk Fuel Dispensing System	\$215,049	\$262,665	\$172,936	\$235,871
Bulk Product Systems	\$730,169	\$732,428	\$499,197	\$672,849
Cab, Climate Control, Instrumentation	\$150,349	\$218,739	\$111,455	\$117,344
Chassis, Axles, Brakes, Frame, Steering, Suspension, Tires & Wheels	\$327,529	\$355,514	\$268,816	\$299,578
Complete Unit	\$410,528	\$413,484	\$325,863	\$403,473
Drive Train (Drive Axles, Clutch, Drive Shafts, Transfer Case, Transmission)	\$861,953	\$1,068,267	\$668,430	\$1,001,488
Electrical (Charging, Cranking, Ignition, Lighting)	\$455,758	\$456,998	\$407,910	\$436,837
Engine (Air Intake, Cooling, Exhaust, Fuel, Power Plant)	\$4,797,295	\$5,004,923	\$4,595,067	\$4,740,758
Equipment Dependent Attachments (Plows, Blades, Buckets, Hydraulics, Etc.)	\$46,935	\$64,156	\$98,521	\$50,728
Heating & Refrigeration	\$1,599,025	\$1,432,672	\$2,041,939	\$1,522,590
Obsolete	\$215,049	\$262,665	\$172,936	\$235,871
Preventative Maintenance Service (All Levels)	\$730,169	\$732,428	\$499,197	\$672,849
Wireless Communication	\$150,349	\$218,739	\$111,455	\$117,344
Grand Total	\$327,529	\$355,514	\$268,816	\$299,578

Table 19. All corrosion-related repair costs of all WSDOT equipment.

All Corrosion	2008	2009	2010	2011
Accessories (Electrical Accessories, Horns & Reverse Alarms, PTO, Winch, Towing Equip, Power Generation, Etc.)	\$ 8,162	\$ 17,621	\$11,895	\$10,761
Body	\$ 9,169	\$37,603	\$19,088	\$ 25,072
Bulk Fuel Dispensing System	\$ 269	\$ 3,119	\$ 685	\$2,292
Bulk Product Systems	\$2,963	\$1,089	\$2,151	\$2,846
Cab, Climate Control, Instrumentation	\$12,224	\$24,798	\$17,730	\$31,610
Chassis, Axles, Brakes, Frame, Steering, Suspension, Tires & Wheels	\$146,743	\$127,214	\$ 115,612	\$155,603
Complete Unit	\$12,042	\$50,033	\$19,181	\$10,939
Drive Train (Drive Axles, Clutch, Drive Shafts, Transfer Case, Transmission)	\$11,279	\$18,882	\$14,564	\$20,990
Electrical (Charging, Cranking, Ignition, Lighting)	\$74,051	\$146,195	\$95,413	\$122,871
Engine (Air Intake, Cooling, Exhaust, Fuel, Power Plant)	\$80,967	\$110,502	\$104,584	\$138,594
Equipment Dependent Attachments (Plows, Blades, Buckets, Hydraulics, Etc.)	\$99,369	\$175,442	\$157,572	\$214,002
Wireless Communication	\$718	\$378	\$41	\$ 519
Grand Total	\$457,956	\$712,969	\$558,516	\$736,362

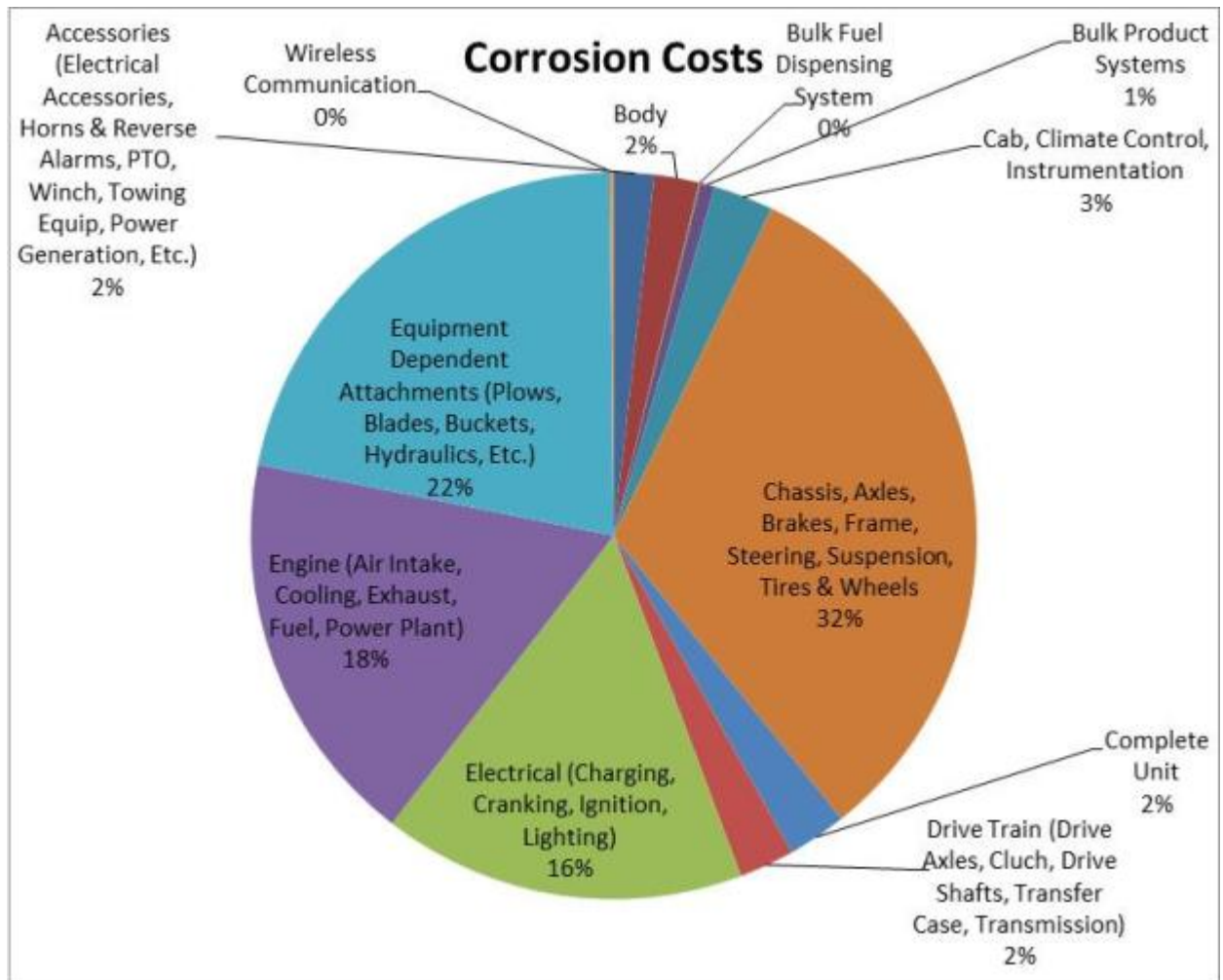


Figure 44. Allocation of corrosion-related repair costs among WSDOT equipment.

Table 20. Total corrosion-related repair cost of WSDOT snowplows.

Class 06 All Corrosion Related Repairs				
	2008	2009	2010	2011
Body	\$27,048	\$88,133	\$39,316	\$43,673
Chassis, Axles, Brakes, Frame	\$129,011	\$98,111	\$77,005	\$113,602
Drive Train (Drive Axles, Clutch, Drive Shafts, Transfer Case, Transmission)	\$10,297	\$16,879	\$11,687	\$15,437
Electrical (Charging, Cranking, Ignition, Lighting)	\$58,601	\$123,656	\$62,981	\$91,657
Engine (Air Intake, Cooling, Exhaust, Fuel, Power Plant)	\$69,657	\$91,899	\$96,236	\$99,177
Equipment Dependent Attachments (Plows, Blades, Buckets, Hydraulics, Etc.)	\$46,336	\$81,737	\$58,585	\$71,083
Total	\$340,950	\$500,415	\$345,810	\$434,629
	2008	2009	2010	2011
Total Repairs Not Counting PM Services	\$4,341,537	\$4,547,925	\$4,187,157	\$4,303,921
Corrosion Related Repairs	\$340,950	\$500,415	\$345,810	\$434,629

3.6. Cost-Benefit Analysis of Mitigating Deicer Corrosion to DOT Equipment

This section will provide an analysis of the direct costs related to metallic corrosion on DOT equipment fleet (including winter maintenance application equipment) aggravated by the exposure to chloride roadway deicers, as well as an analysis of the direct benefits of mitigating such corrosion.

For an “average agency” (e.g., a northern state DOT with an average size of fleet asset), one can assume that it is possible to reduce the total cost of corrosion risks related to deicer exposure by 25%, if the agency can increase its investment in equipment corrosion management by 75% and focus more on proactive maintenance (vs. reactive maintenance). Based on the data in Table 3 and Table 5, the benefit/cost ratio of further improving deicer corrosion management of DOT equipment fleet can be estimated to be: $(25\% \times \$14,084,782) / (75\% \times \$1,063,029) = 4.4$. This ratio is conservative since it does not take into account the indirect costs of equipment corrosion (at least another 20% of the direct costs).

Before proceeding to the case study for the WSDOT, this section will provide an indirect validation of a critical data point from the survey responses, i.e., the deicer corrosion cost due to equipment value depreciation. As shown in Table 5, the equipment value depreciation is the largest and dominant one among the six identified cost items. Table 4 indicates that on average the deicer corrosion leads to a 17.3% reduction in the DOT equipment service life. As a result of metallic corrosion (including those caused by chloride deicers), the Oregon DOT has \$37,000,000 of equipment assets that see a 20% reduction in service life (from 15 years to 12.5 years) and \$2,000,000 of equipment assets that see a 50% reduction in service life (from 20 years to 10 years). To simplify, one can assume that on average a northern DOT's equipment has a 15-year design life but sees a 12-year service life as a result of deicer corrosion. According to Fan et al. (2011), for a heavy vehicle serving in Texas (where deicer exposure is negligible), its (salvage) value can be estimated from the following empirical equation:

$$\text{Salvage Value} = \text{Original Purchasing Price} \times 0.6075 \times e^{(-0.078 \times \text{equipment age})}$$

As such, the depreciation coefficient for DOT equipment in absence of deicer exposure (i.e., over a 15-year service life) is -0.078 and the depreciation coefficient for DOT equipment in the presence of deicer exposure (i.e., over a 12-year service life) is $-0.078 \times 15/12 = -0.0975$, i.e., 25% faster. When there is no deicer-related corrosion and the number of DOT equipment assets is equally distributed among the ages between 0 and 15 years; in this case the average value of DOT equipment assets over a 16-year duration can be estimated from the following equation:

$$\text{Equipment Assets Value} = \text{Original Purchasing Price} \times 0.6075 \times [1 + e^{(-0.078)} + e^{(-0.078 \times 2)} + e^{(-0.078 \times 3)} + \dots + e^{(-0.078 \times 15)}] / 16 = 38.5\% \text{ Original Purchasing Price}$$

When there is deicer-related corrosion and the number of DOT equipment assets is equally distributed among the ages between 0 and 12 years; in this case the average value of DOT equipment assets over a 16-year duration can be estimated from the following equation:

$$\text{Equipment Assets Value} = \text{Original Purchasing Price} \times 0.6075 \times [1 + e^{(-0.0975)} + e^{(-0.0975 \times 2)} + e^{(-0.0975 \times 3)} + \dots + e^{(-0.0975 \times 12)} + 0 + 0 + 0] / 16 = 31.8\% \text{ Original Purchasing Price}$$

Therefore, the change in equipment assets value due to the deicer corrosion can be estimated to be: $(31.8\% - 38.5\%) / 38.5\% = -17.4\%$. This coincides with the average estimate by the survey respondents (17.3% change in equipment value depreciation), as shown in **Table 3**.

Finally, one can proceed to the WSDOT case study. There are three main annual cost numbers estimated from the historical data, i.e., proactive maintenance at \$359,942 (vs. the average value of \$171,424 shown in Table 15), equipment value depreciation at \$29,355,047 (vs. the average value of \$12,512,227 shown in Table 5), and increased premature repair/replacement at \$246,118 (vs. the average value of \$139,224 shown in Table 5). First of all, the number \$359,942 was based on the assumption that 19.6% of the proactive

maintenance cost (Table 4) on the WSDOT equipment fleet (\$1,839,118, in 2011 US dollars) can be attributed to deicer exposure alone. Secondly, the number 29,355,047 was based on the assumption that 17.4% of the equipment value depreciation of WSDOT equipment assets (\$168,558,632, in 2011 US dollars) can be attributed to deicer exposure alone. Finally, a few assumptions are made as follows in order to plot the WSDOT historical data as shown in Figure 41 and to attribute the reasonable portion of corrosion-related repair costs to deicer exposure.

Assumption 1: Calibrated deicer exposure for a given year (e.g., 2008) = Deicer usage in the previous fiscal year (e.g., FY2007) + 50% Deicer usage in the current fiscal year (e.g., FY2008).

Assumption 2: Proactive maintenance of DOT equipment led to cost avoidance, i.e., greatly reduced the corrosion-related repair costs. Calibrated annual corrosion-related repair cost of WSDOT fleet = Recorded cost of “all corrosion related repairs” $\times [1 + (\text{cost of proactive maintenance} / \text{cost of all equipment repairs})^{0.2}] \times [(1 + 10\%)^n]$. This normalizes all cost numbers in 2011 U.S. dollars, with 10% being the assumed inflation rate and n being 0, 1, 2, and 3 for year 2011, 2010, 2009, and 2008 respectively.

Assumption 3: For the conceptual scenario of “no deicer exposure and no proactive maintenance”, the cost of “all corrosion related repairs” for all DOT equipment is assumed to be 19.6% less than the actual number recorded in the year the least amount of deicer was applied (i.e., year 2008). On the other hand, the cost of “all corrosion related repairs” for all DOT equipment is assumed to be $19.6\% \times (\text{Cost of snowplow corrosion-related repairs} / \text{Cost of snowplow all repairs}) / (\text{Cost of all equipment corrosion-related repairs} / \text{Cost of all equipment all repairs}) = 19.6\% \times 9.3\% / 4.3\% = 42.2\%$ less than the actual number recorded in year 2008.

Therefore, in year 2011, the deicer-corrosion-related repairs of all WSDOT equipment is estimated to be $\$736,362 - \$490,244 = \$246,118$ (in 2011 U.S. dollars).

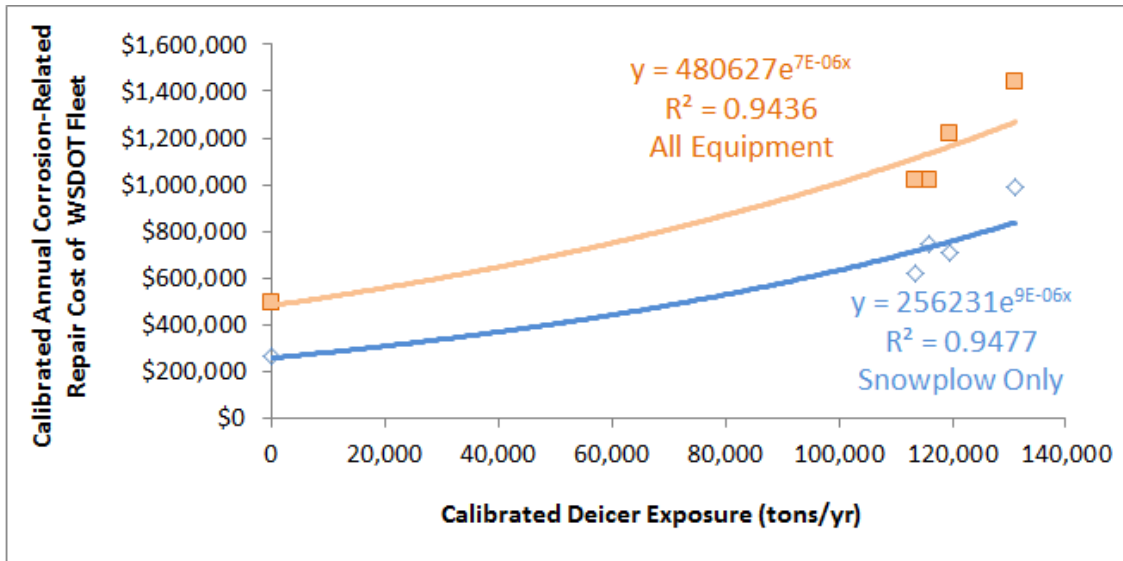


Figure 45. Correlating the annual corrosion-related repair cost (in 2011 U.S dollars) with the level of deicer exposure.

For the WSDOT (with an equipment asset of \$168,558,632), one can assume that it is possible to reduce the total cost of corrosion risks related to deicer exposure by 20%, if WSDOT can increase its investment in equipment corrosion management by 75% and focus more on proactive maintenance (vs. reactive maintenance). As such, the benefit/cost ratio of further improving deicer corrosion management of DOT equipment fleet can be estimated to be: $(20\% \times \text{approximately } \$30 \text{ million}) / (75\% \times \text{approximately } \$1 \text{ million}) = 8$. This ratio is conservative since it does not take into account the indirect costs of equipment corrosion (at least another 20% of the direct costs).

CHAPTER 4 - CONCLUSIONS

4.1. Conclusions

From the published literature, it is clear that the corrosion-related deterioration and damage is a major durability concern for assets in many industries. Deicer-induced corrosion may affect the performance and service life of metallic components, electrical connections, joint connections, hydraulic systems, bearings, engine components, etc. The corrosion of motor vehicles due to road salts was estimated to cost \$2.8 billion to \$5.6 billion per year. The literature review has focused on the metals commonly seen in DOT vehicles and equipment, including: steels, aluminum/aluminum alloys, magnesium alloys, zinc, and cast irons. Different metals have inherently different characteristics and they may differ greatly in their type and extent of corrosion in the service environment. The corrosion of metals in equipment can be mitigated through better material selection, improved design, proactive or reactive maintenance practices.

The survey results suggest that chloride-based deicers are the most commonly used products for highway winter maintenance operations and pose significant corrosion risk to DOT equipment and vehicles. The survey results show that chloride deicers pose the most significant risk of metallic corrosion to dump trucks followed by liquid deicer applicators, front end loaders and hoppers. Most metallic components on vehicles and equipment are very vulnerable to chloride deicer corrosion, and this risk is especially high for electrical wiring, frames, brackets and supports, brake air cans, brake drums and disks, spreader chute, fittings, and granular hopper. Cast irons have seen the most serious general corrosion, followed by carbon steels, composites, and magnesium alloys. Aluminum alloys and stainless steels have seen the most serious localized corrosion, followed by metallic glass, metallic coatings, and magnesium alloys.

The agency survey identified annual expenditures in the current practices of managing deicer-related metallic corrosion in the equipment fleet of responding agencies that report it as being a significant issue. The findings are summarized as follows.

	Training programs	Materials selection	Design improvements	Corrosion monitoring /testing	Proactive maintenance	Reactive maintenance
No. of Responses	8	15	9	1	14	8
Average	\$190,938	\$320,667	\$45,000	\$10,000	\$171,424	\$325,000
Standard Deviation	\$342,845	\$568,651	\$43,157	NA	\$279,106	\$319,598
Coefficient of Variance	180%	177%	96%	NA	163%	98%

The agency survey also identified the current risks and annual costs of deicer corrosion to the equipment fleet of responding agencies that report it as being a significant issue, estimated under the current level of corrosion management. The findings are summarized as follows.

	Depreciation in value	Increased downtime	Reduced reliability	Reduced service life	Increased premature repair and replacement	Safety risk due to faulty parts
No. of Responses	12	13	9	12	7	4
Average	17.3%	8.5%	11.9%	17.3%	19.6%	1.5%
Standard Deviation	12.6%	8.3%	8.7%	12.6%	12.2%	1.0%
Coefficient of Variance	73%	98%	74%	73%	62%	67%

	Depreciation in value	Increased downtime	Reduced reliability	Reduced service life	Increased premature repair and replacement	Safety risk due to faulty parts
No. of Responses	9	6	5	4	5	1
Average	\$12,512,227	\$69,167	\$172,000	\$1,127,750	\$139,224	\$30,000
Standard Deviation	\$27,053,553	\$94,943	\$205,597	\$1,121,133	\$72,729	NA
Coefficient of Variance	216%	137%	120%	99%	52%	NA

The survey and literature review identified four anti-corrosion coating products (Zero Rust Red, Zero Rust Black, Rust Bullet and Lubra-Seal), four spray-on corrosion inhibitors (Krown, Ship-2-Shore, Vegetable Oil and Rust Oleum), and six salt removers (MR 35, HoldTight, ChloRid, SaltAway, Soap Water, and Neutro-Wash) as best products against deicer corrosion to equipment. Subsequently, a screening test and a 2-week test were conducted to assess the effectiveness of these select products in reducing the corrosion of magnesium chloride solution to carbon steel, using electrochemical impedance spectroscopy (EIS) measurements. Under the investigated conditions, the best-performing coating (*Rust Bullet*), spray-on corrosion inhibitor (*Krown*) and salt removers (*HoldTight* and *ChlorRid*) were identified and they all showed outstanding performance in providing corrosion protection to the carbon steel substrate against $MgCl_2$ solutions. From the wet-dry test, it can be concluded that the power-washing with salt remover *HoldTight* (to a less extent, soapy water) can significantly enhance the anti-corrosion property of carbon steel (1008 CS) and stainless steel (204 SS) in $MgCl_2$ solutions. However, no significant benefits were observed from power-washing with *HoldTight* in protecting the aluminum alloy (1100 Al) against corrosion by $MgCl_2$. The data also imply that once active corrosion of metals started, the benefits of simply power-washing in reducing the corrosion rate of metals would diminish.

Environment exposure studies were performed by the Southwest Research Institute® (SwRI®) to further investigate the potential benefits of select corrosion inhibitors and anti-corrosion coating in mitigating the deicer corrosion of vehicle component materials. *In situ* corrosion data, including both general and maximum localized corrosion rates, acquired from each multi-electrode array sensor (MAS) are used to assess the corrosion inhibition in an accelerating manner.

- MAS was found to be an effective tool to *in situ* characterize corrosion of Al, SS, and SS materials in cyclic exposure environments, in the presence of corrosive deicer agents.
- For all three materials in both MgCl₂ and NaCl exposure environments, the most severe corrosion occurred at the beginning of humid stage. Therefore, reducing dry-wet exposure cycles will effectively decrease material corrosion, especially localized corrosion. Even though the cyclic exposure to diluted MgCl₂ poses more corrosion risk to 314 SS and 1008 CS than that to diluted NaCl, such risks are better mitigated by the spray-on corrosion inhibitors tested.
- Periodically spraying a corrosion inhibitor (*Krown T40*, 19 times per year) would effectively protect the aluminum, stainless steel, and carbon steel components on DOT equipment from corrosion related to NaCl or MgCl₂ deicers, by reducing their corrosion rate by at least 99%. Similarly, a one-time application of protective coating (*Rust Bullet*) reduced their corrosion rate by at least 99.5%, but additional research is needed to improve the integrity and durability of such coating over the years of field exposure.

For the entire WSDOT fleet, the corrosion-related repair costs and preventative maintenance (PM) costs averaged 4.3% and 12.9% of the all repair costs (excluding PM costs), respectively. For the WSDOT snowplows, the corrosion-related repair costs and PM costs averaged 9.3% and 10.1% of the all repair costs (excluding PM costs), respectively. This highlights the fact that snowplows tend to corrode much faster than other WSDOT equipment, likely due to their more extensive exposure to roadway deicers.

For an “average agency” (e.g., a northern state DOT with an average size of fleet asset), one can assume that it is possible to reduce the total cost of corrosion risks related to deicer exposure by 25%, if the agency can increase its investment in equipment corrosion management by 75% and focus more on proactive maintenance (vs. reactive maintenance). As such, the benefit/cost ratio of further improving deicer corrosion management of DOT equipment fleet can be estimated to be: $(25\% \times \$14,084,782) / (75\% \times \$1,063,029) = 4.4$. This ratio is conservative since it does not take into account the indirect costs of equipment corrosion (at least another 20% of the direct costs).

For the WSDOT (with an equipment asset of \$168,558,632), one can assume that it is possible to reduce the total cost of corrosion risks related to deicer exposure by 20%, if WSDOT can increase its investment in equipment corrosion management by 75% and focus more on proactive maintenance (vs. reactive maintenance). As such, the benefit/cost ratio of further improving deicer corrosion management of DOT equipment fleet can be estimated to be: $(20\% \times \text{approximately } \$30 \text{ million}) / (75\% \times \text{approximately } \$1 \text{ million}) = 8$. This ratio is conservative since it does not take into account the indirect costs of equipment corrosion (at least another 20% of the direct costs).

4.2. Implementation Recommendations

In light of the research findings from this project, we provide the following recommendations for implementation:

1. Wherever possible, agencies should consider using corrosion-inhibited products or non-chemical means (e.g., pavement technologies) for snow and ice control, so as to reduce the deicer corrosion to DOT equipment, other vehicles, and possibly transportation infrastructure. This recommendation is based solely on the corrosion risk inherent in chloride deicers, and does not consider other dimensions of the deicer usage such as cost, performance, and chlorides or abrasives loading in water bodies.

2. Agencies should consider corrosion-resistance requirements at the stages of materials selection and design. Existing knowledge about the anti-corrosion performance of various materials and design configurations in various deicer-laden service environments should be utilized to refine the equipment purchasing specifications developed by the transportation agencies. For instance, the zinc coating on steel substrates can provide good anti-corrosion performance. Structures designed for resistance to atmospheric corrosion should always provide easy drainage from all exposed surfaces. Stress corrosion cracking (SCC) can be prevented by substituting a more resistant alloy, removing the tensile stress, or making the environment less aggressive. Crevice corrosion can be minimized by proper design of welded joints and gaskets that minimize crevices. Contact between dissimilar metals can lead to galvanic corrosion and should be avoided wherever possible. Alternatively, modifications should be made to DOT equipment to mitigate the risk of deicer corrosion. For instance, WSDOT implemented the following best practices: use of high-quality weather-proof terminations (e.g., buss-style connectors and compression fittings) in equipment specifications; elimination of junction boxes wherever possible, relocation of junction boxes to inside the cab off the floor; use of sealed brake canisters and sealed protective boxes surrounding hydraulic components and batteries; and, use of high-quality weather-proof terminations and compression fittings in addition to shrink wrapping susceptible electrical wiring components. Some additional best practices by others: eliminating areas that solids and liquids may accumulate; specifying rust-proof brake shoes when rebuilding; specifying self-healing undercoats for chassis; specifying fender liners for chassis; using dielectric silicone for sealing damaged areas or connections; opening up closed areas (e.g. pillars) and allowing them to flush out easily; using welds to close and seal off certain areas that are difficult to drain; caulking welds prior to painting; avoiding any damage of wiring insulation; etc. Finally, certain corrosion-prone components should use corrosion-resistant materials (e.g., stainless steel or non-metallic) or be inspected and replaced on a regular basis (e.g., replacing truck radiators every two years).

3. Wherever possible, agencies should consider de-humidified storage of their equipment and vehicles. Or at least store equipment in dry climate after washing. This is expected to minimize the risk of metallic corrosion and extend the service life of equipment and vehicles. Relative to NaCl, MgCl₂ and CaCl₂ are more hygroscopic and thus their residue on the bare metals in the equipment can lead to higher risk of corrosion, even in seemingly dry environments (e.g., RH of 35%).

4. Agencies should implement an extensive preventative maintenance program to preserve the value and performance of their equipment and vehicles. For instance, WSDOT implemented the following best practices: consistent washing after application, regular rinsing and localized cleaning (followed by fast drying), using high-quality primers and topcoats in equipment specifications, using composite materials less susceptible to corrosion, and protecting new and replacement components prior to installation with wraps, covers, or shields. Power-wash with salt remover *HoldTight* or similar product to significantly enhance the anti-corrosion property of carbon steel and stainless steel parts against deicer corrosion. Once active corrosion of metals started, power-washing should be coupled with other means, e.g., applying spray-on corrosion inhibitor (e.g., *Krown T40*, 19 times per year) immediately after the equipment is washed clean and dried. Other methods of aftermarket rust-proofing may include the application of post-assembly coatings (e.g., *Rust Bullet*).

5. Agencies should implement reactive maintenance practices to minimize the negative impact of deicer corrosion to their equipment and vehicles. For instance, WSDOT implemented the following best practices: neutralizing the existing corrosion (e.g., via abrasive blasting and steam cleaning and/or chloride neutralizer spray) and cleaning the area or material that was corroded.

6. Agencies should track the data relevant to analyzing the direct costs of deicer corrosion to their equipment asset and the direct benefits of countermeasures, so as to enable reliable, quantitative cost-benefit analysis. Currently, there is a clear absence of documented information, both in the published literature and in the practitioner community that spells out such quantified values. Regardless of the issues that may be inherent to specific items, agencies should consider revising the corrosion management information they currently collect if a more rigorous understanding of the costs and benefits associated with deicer corrosion to equipment is desired.

7. Additional research is recommended to bridge some existing knowledge gaps relevant to this subject. First of all, research is needed to optimize the use of best practices or products for corrosion protection of vehicles and equipment and to evaluate their long-term effectiveness. For instance, there is currently a lack of information on the cost-effectiveness of automated internal washing mechanisms and other effective washing techniques, relative to a low-volume high-pressure washing system. It is desirable to test the field performance of regular washing (with salt remover) and innovative anti-corrosion products. For instance, there is lack of field testing of products (such as ECK[®]) that claim to “offer a barrier between dissimilar metals, seal out moisture, and ...eliminate corrosion between aluminum and SS fasteners”; or water-based biodegradable rust removers or rust converters (e.g., Bio-Rust[®]) that claim to “allow a relatively inexpensive method of significantly improving the quality of the metal surface and ...improve lifetime of the coating”. Secondly, additional research should be conducted to explore methods to minimize the risk of premature failure of the post-assembly coatings (e.g., *Rust Bullet*), both on boldly exposed surfaces and within occluded sites. Thirdly, research is needed to assess the effectiveness and benefits in the synergistic use of frequent washing, salt remover, corrosion inhibitor, and possibly coating to protect the DOT equipment. Fourthly, research is needed to identify, develop, and evaluate technologies

to on-line assess the condition of key metallic components and their applied coatings so that maintenance of the metal or coating can be performed based on the corrosion condition. For instance, corrosion sensors can alert maintenance personnel in real time if the coating at a specific location on certain equipment falls below a predetermined threshold or is diagnosed to have failed, triggering a timely maintenance action. Such technologies can provide the basis for a corrosion management and planning tool for equipment fleet managers. It will also be possible to provide the maintenance engineers and equipment owners with a long-term record of the equipment's condition, which can be examined along with the history of the equipment itself and the exposure conditions it experiences. Such knowledge would serve as the basis of "best practice" guidelines for design and maintenance of the equipment. Finally, research is needed to develop best practice guidelines (e.g., a user's corrosion management guide) once laboratory and field studies are conducted to validate the best practices against deicer corrosion.

Such research will benefit DOTs as well as other owners of equipment that is at risk of metallic corrosion. By identifying preventive measures and techniques, the service life of DOT equipment fleet can be prolonged and repairs can be reduced, resulting in cost savings to the agency. The main audience of such research will be DOT equipment engineers and managers. Other stakeholders may include: equipment manufacturers, trucking associations, winter road maintenance practitioners, etc. Overall, the findings are expected to modify the approach to equipment asset management by DOTs and other agencies and enable them to make informed or better choices on preserving the quality and life of equipment assets. Condition-based maintenance strategies can be used to reduce inspection and maintenance costs, while minimizing the risk of equipment damage or failure due to corrosion and maximizing equipment readiness and performance.

REFERENCES

- [1] Menzies, T.R. National Cost of Motor Vehicle Corrosion From Deicing Salt. Proceedings of the CORROSION/91 Symposium “Automotive Corrosion and Protection”. Editor: Robert Baboian. Published by NACE. Houston, TX, 1992. pp. 1-1.
- [2] Johnson, J.T. Corrosion costs of motor vehicles, 2002.
<http://www.corrosioncost.com/pdf/transportation.pdf>, accessed in July 2007.
- [3] Rendahl, N., Hedlund, S. The Influence of Road Deicing Salts on Motor Vehicle Corrosion. Proceedings of the CORROSION/91 Symposium “Automotive Corrosion and Protection”. Editor: Robert Baboian. Published by NACE. Houston, TX, 1992. pp. 5-1.
- [4] Levelton Consultants Ltd. Guidelines for the selection of snow and ice control materials to mitigate environmental impacts. NCHRP Report 577. National Cooperative Highway Research Program, National Research Council, Washington, D.C., 2008.
http://onlinepubs.trb.org/onlinepubs/nchrp/nchrp_rpt_577.pdf, accessed in July 2008.
- [5] Western Transportation Institute (WTI). Preliminary Corrosion Investigation for Bill Field Trucking Company: Is Deicer the Culprit? Internal email communications. Montana State University. Bozeman, MT, 2005.
- [6] Stephens, E., Pitman, S., Mattlin, K., Chamberlin, C., Dahl, M. “Effects of Highway Ice-Clearing Treatments on Corrosion of Heavy Vehicle Materials and Components”. A presentation by Pacific Northwest National Laboratory for the Pacific Northwest Snowfighters Conference, June 15, 2006. PNNL-SA-50448.
- [7] Snow and Ice Related Corrosion and Its Effect on Equipment: How Do We Cope. Washington State Department of Transportation. A presentation for the Northwest Snowfighters Conference, 2008.
<http://www.wsdot.wa.gov/partners/pns/pdf/presentations/SnowandIceRelatedCorrosion.pdf>
- [8] Fay, L, K. Volkening, C. Gallaway, and X. Shi. Performance and impacts of current deicing and anti-icing products: user perspective versus experimental data. TRB 87th Annual Meeting Compendium of Papers DVD, Transportation Research Board, Washington D.C., January 2008, Paper number 08-1382.
- [9] Salt Institute. <http://www.saltinstitute.org/33>. Accessed October 22, 2008.
- [10] Fay, L., Shi, X. Environmental Impacts of Chemicals for Snow and Ice Control: State of the Knowledge. *Water, Air & Soil Pollution*, 2012, No.223, pp.2751–2770.
- [11] *Corrosion costs and preventative strategies in the United States*. Federal Highway Administration, Publication No. FHWA-RD-01-156, 2002.
- [12] Shi, X., Fay, L., Yang, Z., Nguyen, T.A., and Liu, Y. *Corrosion Reviews*, Vol. 27, No. 1-2, 2009, pp. 23-52.

- [13] Amrhein, C., J.E. Strong and P.A. Mosher, *Environm. Sci. Tech.*, Vol. 26, No. 4, 1992, pp. 703-709.
- [14] Thompson, N.G., M. Yunovich, D. Dunmire, *Corrosion Review*, Vol. 25, No. 3-4, 2007, pp. 247.
- [15] Preliminary Corrosion Investigation for Bill Field Trucking Company: Is Deicer the Culprit? Internal report. Western Transportation Institute (WTI), Montana State University. Bozeman, MT, 2005.
- [16] Uchida, M., K. Mochizuki, *Kawasaki Steel Giho*, Vol. 32, No. 1, 2000, pp. 26.
- [17] Jones, D. A. *Principles and Prevention of Corrosion*. 2nd Ed. Prentice Hall, NJ, USA, 1996.
- [18] Palle, S., R. Younce, T. Hopwood II. *Investigation of Soluble Salts on Kentucky Bridges*. Research Report (KTC-03-02/UI 4-02-1F), Kentucky Transportation Center, 2003.
- [19] Menzies, T.R. National Cost of Motor Vehicle Corrosion From Deicing Salt. *Automotive Corrosion and Protection*. Proceedings of the CORROSION/91 Symposium. Editor: Robert Baboian. Published by NACE. Houston, TX, 1992. pp. 1-1.
- [20] Johnson, J.T. *Corrosion costs of motor vehicles*, 2002.
<http://www.corrosioncost.com/pdf/transportation.pdf>, accessed in July 2007.
- [21] Wei, B. Theories and Applications of Metallic Corrosion. 1st Ed. Chem. Eng. Press, Beijing, China, 1984.
- [22] Jones, D. A.. *Principles and Prevention of Corrosion*. 2nd Ed. Prentice Hall, NJ, USA, 1996.
- [23] Nixon, W. A. and Xiong, J. Investigation of Materials for the Reduction and Prevention of Corrosion on Highway Maintenance Equipment. Iowa Highway Research Board. IIHR Technical Report # 472. May 2009.
- [24] Morrison, D. Study of Corrosion Protection Methods for GSE Applications at Kennedy Space Center. Materials Testing Branch, Kennedy Space Center, Florida. Study report number MAB 3221-69. May 1972.
- [25] Palmer, J.D. Current Public Interest Aspect of Automotive Corrosion. Proceedings of the CORROSION/91 Symposium "Automotive Corrosion and Protection". Editor: Robert Baboian. Published by NACE. Houston, TX, 1992. pp.4-1.
- [26] Payer, J.H. Effect of Environmental Stress on Reliability of Automotive Electronics. Proceedings of the CORROSION/91 Symposium "Automotive Corrosion and Protection". Editor: Robert Baboian. Published by NACE. Houston, TX, 1992. pp.11-1.
- [27] Lazarevic, Z. Z., Miskovic-Stankovic, V. B., Kacarevic-Popovic, Z., Drazic, D. M. *Corros. Sci.* 47 (3) (2005) 823.
- [28] Shi, X., Nguyen, T. A., Suo, Z., Liu, Y., Avci, R. *Surface & Coatings Technology* 204 (2009) 237.

- [29] American Public Works Association Research Foundation. (1970). Vehicle Corrosion Caused by Deicing Salts: Evaluation of the Effects of Regular vs. Inhibited Salt on Motor Vehicles. Report No. APWA-SR-34.
- [30] Fan, W., Machemehl, R.B., and Kortum, K. (2011). "Equipment Replacement Optimization: Solution Methodology, Statistical Data Analysis, and Cost Forecasting". Transportation Research Record: Journal of the Transportation Research Board, No. 2220, pp. 88-98.
- [31] Shi, X., Nguyen, T.A., Suo, Z., Liu, Y., and Avci, R. (2009). "Effect of Nanoparticles on the Anticorrosion and Mechanical Properties of Epoxy Coating". Surface and Coatings Technology 204(3), 237-245.
- [32] Stephens, E., Pitman, S., Mattlin, K., Chamberlin, C., and Dahl, M. (2006). "Effects of Highway Ice-Clearing Treatments on Corrosion of Heavy Vehicle Materials and Components". A presentation by Pacific Northwest National Laboratory for the Pacific Northwest Snowfighters Conference, June 15, 2006. PNNL-SA-50448.
- [33] Wang, Y., Underhill, R.S., and Klassen, B. (2006). Review of corrosion control programs and research activities for army vehicles. Defense R&D Canada – Atlantic. Technical Memorandum. DRDC Atlantic TM 2006-055. <http://pubs.drdc.gc.ca/PDFS/unc53/p526285.pdf>, accessed in July 2008.
- [34] Hora, S., Miura, M., Uchiumi, Y., Fujiwara, T., and Yamamoto, M. (2005). "Suppression of Deicing Salt Corrosion of Weathering Steel Bridges by Washing". Corrosion Science, Vol. 47, pp. 2419-2430.
- [35] Dean, W.P., Sanford, B.J., Wright, M.R., and Evans, J. L. (2012). "Influence of De-icers on the Corrosion and Fatigue Behavior of 4140 Steel". Journal of Materials Engineering and Performance, DOI: 10.1007/s11665-012-0167-6.
- [36] Morrison, D. (1972). Study of Corrosion Protection Methods for GSE Applications at Kennedy Space Center. Materials Testing Branch, Kennedy Space Center, Florida. Study report number MAB 3221-69.
- [37] Palmer, J.D. (1992). Current Public Interest Aspect of Automotive Corrosion. Proceedings of the CORROSION/91 Symposium "Automotive Corrosion and Protection". Editor: Robert Baboian. Published by NACE. Houston, TX, 1992.
- [38] Payer, J.H. (1992). Effect of Environmental Stress on Reliability of Automotive Electronics. Proceedings of the CORROSION/91 Symposium "Automotive Corrosion and Protection". Editor: Robert Baboian. Published by NACE. Houston, TX, 1992.
- [39] Washington State Department of Transportation (2008). "Snow and Ice Related Corrosion and Its Effect on Equipment: How Do We Cope". A presentation for the 2008 Pacific Northwest Snowfighters Conference. <http://www.wsdot.wa.gov/partners/pns/pdf/presentations/SnowandIceRelatedCorrosion.pdf>.

APPENDICES

Preceding sections of the final report have been directed to practitioners, public officials, and administrators. Appendix presentations are designed for the researcher, developer of manuals and guidelines, and other professional users of the research results who are interested in the maximum degree of technical detail provided by the project effort.

Appendix A: Literature Review

Chapter 1 Corrosion Cost Analysis

The damage of corrosion have caused is becoming a major issue in our society. The cost that used to cure corrosion is not decreasing but increase every year due to diversity of chemical compounds had been discovered and used in the environment.

1. Cost of Corrosion

Corrosion is a natural process that compromises the material's integrity and thus impacts assets, environment, and people. A historic congressional study in 2002 estimated metallic corrosion was approximated to be \$276 billion annually for the US. The direct cost of corrosion to the US infrastructure and transportation system was estimated at \$52.3 billion annually. It has been estimated that the indirect costs of corrosion are at least equal to or greater than the direct cost (**Thompson et al., 2007**).

Table 1. Industries that affected by the cost of corrosion

	Cost (\$)	References
U.S military	10 to 20 billion annually	(Thompson et al., 2007)
International Air Transport Association(IATA)	8 to 20 per flight hour	(Adjorlolo and Marceau, 2005).
Automobiles	2.5 billion improvement of corrosion resistance 6.5 billion maintenance and repairs 14.4 billion depreciation	(Johnson, 2002).

From Table 1, it can be seen that many industries are affected by the cost of corrosion including the US military which spends an estimated \$10 to \$20 billion annually (**Thompson et al., 2007**). In 1983 the International Air Transport Association (IATA) stated that the airlines cost of corrosion was between \$8 and \$20 per flight hour, which did not include the unscheduled downtime due to corrosion inspections (**Adjorlolo and Marceau, 2005**). In 1975, the Battelle-NBS study estimated the total cost of corrosion in the US to be \$70 billion. The estimated cost of corrosion related to automobiles was \$23.4 billion; of which \$2.5 billion was associated with necessary manufacturing changes to improve corrosion resistance, \$6.5 billion was attributed to maintenance and repairs, and the final \$14.4 billion was due to depreciation caused by corrosion (**Johnson, 2002**).

Moreover, the U.S. applies approximately 15 million tons of salts each year (**Salt Institute, 2005**) and spends \$2.3 billion annually to keep roads clear of snow and ice (**Federal Highway Administration, 2005**), which translates into average nominal cost of \$153 per ton for salting. Such maintenance activities are essential to maintain winter roadway safety, mobility and productivity (**Institute for Safety Analysis, 1976; Marquette University, 1992**), but the use of chemicals has raised concerns about their effects on motor vehicles, the transportation infrastructure, and the environment (**Federal Highway Administration, 2002; Mussato et al., 2003; Buckler and Granato, 1999**). One study estimates that road salt imposes infrastructure corrosion costs of at least \$615 per ton, vehicular corrosion costs of at least \$113 per ton, aesthetic costs of \$75 per ton if applied near environmentally sensitive areas, plus uncertain human health costs (**Vitaliano, D., 1992**). Another conservative estimate of the cost of corrosion damage to vehicles due to road salt was found to be \$2.04 billion per year or \$136 per ton of road salts used (**Menzies, T.R., 1991**). For example, in

the state of New York, the NYDOT estimated a cost of \$113 per ton of salt used with an annual cost of \$45 million per year (**Vitaliano, 1992**).

The cost of corrosion could be decreased as the applications of improved designs are implemented. Industry experts believe that the application of current day, leading edge, engineering practices and anticorrosion technology could reduce corrosion costs from 25% to 30%. With the advancement of science and engineering and the application of leading edge methods and technology, it is projected that an estimated 50% savings in corrosion costs can be achieved by the years 2030-2040 (**Thompson et al., 2007**).

In order to reduce the costs associated with corrosion, the following actions can be taken: spread information about the costs of corrosion and the possible savings, make the public aware of ways to prevent corrosion, improve designs to achieve better corrosion resistance, modify practices and policies to increase savings, improve corrosion modeling and prediction methods, improve technology through research and development, and increase education and training on corrosion prevention (**Johnson, 2002**).

2. Corrosion-Prone Parts

Sites likely to exhibit corrosion are areas where dirt and other material deposit and remain wet including metal folds and joints, breaks in painted surfaces, threaded-screws, and beneath coatings that do not adhere well to the surface beneath (**Baldi et al., 1989**).

The structural components of the underbody are normally composed of low carbon steel and high strength steel. These underbody components commonly experience pitting, crevice, galvanic, and cosmetic corrosion. Pitting corrosion is a localized attack, often caused by chlorides, which result in a roughened surface. Crevice corrosion occurs when an electrolyte is trapped in joints, crevices, poutices, or under deposits. Galvanic corrosion occurs where different types of metals come in contact with one another. Cosmetic corrosion often originates where the coating or paint is damaged or penetrated. The damage to the visible surface is usually just visual but in some cases is more severe (**Berg et al, 1999**).

The recent increase in the production of corrosion preventative products for semi-trucks has caused a rise in concern about the integrity of the following components prone to corrosion: brake shoes, trailer underbodies, trailer landing gear, junction boxes, door headers, sills, bulk heads, mud flap brackets, threshold plates, logistics posts, and roof bows (**Hartley, 2010**). For example, five of the major vehicle manufacturers have recalled about 7.4 million vehicles in the last couple years due to premature corrosion of vehicle safety components caused by deicers, including: brake line malfunctioning, deterioration of the axle, steering issues, and problems with the gas tank (**Cornwell, 2011**).

3. Concluding Remarks

In this chapter, we have discussed some examples regard to cost of corrosion and corrosion prone parts. From those examples we can see that the cost of corrosion is already become a big role of economy spending in many industries including U.S military, DOTs and major airlines. On the other hand, different types of corrosion are also been discovered recently due to increasing of use chemicals in our society. The importance of develop materials that can resist corrosion or chemical compound that result less corrosion to metals are becoming critical and they will result a significant reduction in the cost of corrosion.

References

- Adjorlolo, A. A., Marceau, J. A., 2005. "Commercial Aircraft." Corrosion Tests and Standards: Application and Interpretation-Second Edition, 687-692.
- Baldi, A. L., Crombie, E. A., Dillard, D. P., Handsy, I. C., 1989. "Development of a Computerized Data Base to Monitor Wheeled Vehicle Corrosion." Research, Development and Engineering Center Technical Report.
- Berg, R. et al, 1999. A Guide to Corrosion Protection.
- Buckler, D.R. and Granato, G.E. 1999. "Assessing Biological Effects from Highway runoff Constituents." U.S. Department of Interior and U.S. Geological Survey Open-File Report. pp. 99-240.
- Cornwell, M., 2011. "Michigan Road Salts: What Is It Costing Us." Michigan Science, 16, 7-8.
- Federal Highway Administration, 2002. "Corrosion Costs and Preventative Strategies in the United States." Publication No. FHWA-RD-01-156
- Hartley, P., 2010. "Corrosion Protection." Fleet Equipment, 16-18.
- Institute for Safety Analysis, 1976. "Benefits and Costs in the Use of Salt to Deice Highways." U.S. Department of Transportation, Washington, D.C.
- Johnson, J.T., 2002, "Corrosion costs of motor vehicles," <http://www.corrosioncost.com/pdf/transportation.pdf>, accessed in July 2007.
- Marquette University, 1992. Accident Analysis of Ice Control Operations.
- Menzies, T.R., 1991. "National Cost of Motor Vehicle Corrosion From Deicing Salts." Paper 91399, National Association of Corrosion Engineers Annual Meeting.
- Mussato, B.T. et al., 2003. "Guidelines for the Selection of Snow and Ice Control Materials to Mitigate Environmental Impacts." Prepared for the NCHRP Project 6-16.
- Salt Institute, 2005. "Highway Deicing and Anti-icing for Safety and Mobility." <http://www.saltinstitute.org/30.html>. Last accessed: May 3, 2005.
- Shi, X. 2005. "The Use of Road Salts for Highway Winter Maintenance: An Asset Management Perspective." *2005 ITE District 6 Annual Meeting*. Kalispell, Montana. July 10-13.
- Thompson, N. G., Yunovich, M., Dunmire, D., 2007. "Cost of Corrosion and Corrosion Maintenance Strategies." Corrosion Reviews, 25 (3-4), 247-261.
- Vitaliano, D., 1992. Economic Assessment of the Social Costs of Highway Salting and the Efficiency of Substituting a New Deicing Material. Journal of Policy Analysis and Management, Vol. 11, No. 3, pp. 397-418.

Chapter 2 Corrosion Mechanisms and Effect of Deicer Corrosion on Metals

There are numerous types of corrosion existing in our society and the damages they had done are extreme. In this chapter, we will discuss some most common corrosion that have had affected metal in the environment associated with neutral pH ($6 < \text{pH} < 8$) and regular temperature ($5^\circ\text{C} - 40^\circ\text{C}$). However, there are many other types of corrosion in varies of condition are urgent to be defined and solved.

1. Types of corrosion

Corrosion, a wearing a way of metal process, occurs when metals in the presence of corrosive environments, undergo chemical reactions that reduce the metals to their more natural forms. The substance formed during corrosion is the corrosion product and the portion of the metal on which corrosion occurred has therefore been corroded. There are many types of corrosion, the two main categories are general corrosion and localized corrosion. General or uniform corrosion occurs over a substantial amount of the metals surface and is the most predictable type. Localized corrosion, on the other hand, is the attack of specific areas of a metal and it is difficult to predict and mode. Scheme 1 is a brief summary of corrosion types in this chapter and the descriptions of each kind of corrosion are given according to Xie and Guthrie's reports. (Xi and Xie, 2002; Guthrie et al., 2002)

-Crevice corrosion occurs at the interface of a metal and another surface, often where a confined or stationary area is formed. Commonly this is observed beneath surface deposits, seals, gaskets, washers, clamps, sleeves, and similar junctions.

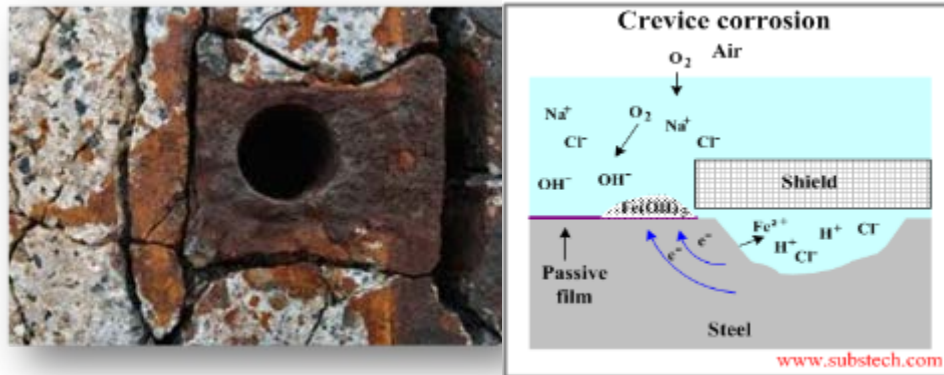


Figure 1 Crevice corrosion (Kopeliovich, 2009)

-Pitting corrosion is often localized on the metals surface and is often difficult to detect due to its relatively small amount of metal loss.

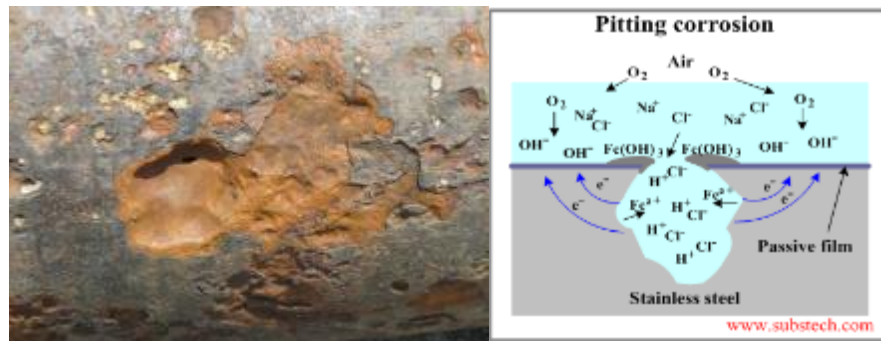


Figure 2 Pitting corrosion (Kopeliovich, 2009)

-Intergranular corrosion occurs at grain boundaries and often spreads along adjacent grain boundaries.

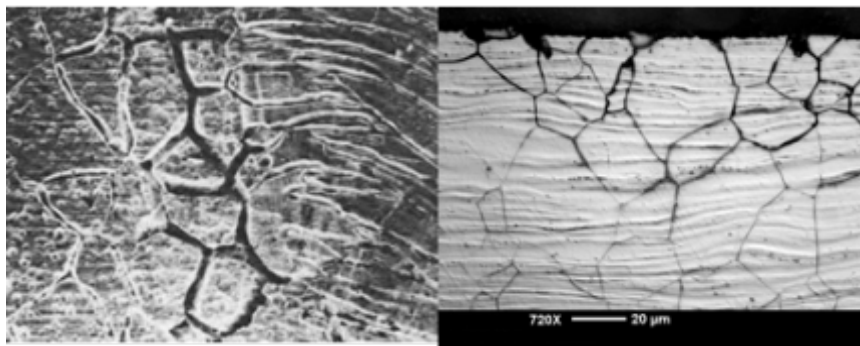


Figure 3 Intergranular corrosion (Kopeliovich, 2009)

-Galvanic corrosion occurs when two different metals are in contact with one another in the presence of an electrolyte, causing an electrochemical reaction to occur. In this reaction current flows from the metal acting as the anode to the metal acting as the cathode.

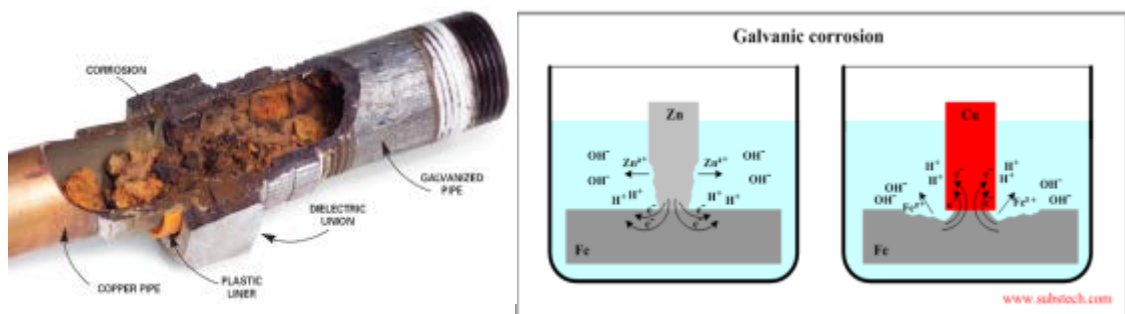


Figure 4 Galvanic corrosion (Kopeliovich, 2009)

-Stress corrosion is the result of applied mechanical stress and corrosion. The presence of residual stresses due to manufacturing processes and corrosion fatigue due to cyclic loading are common causes.

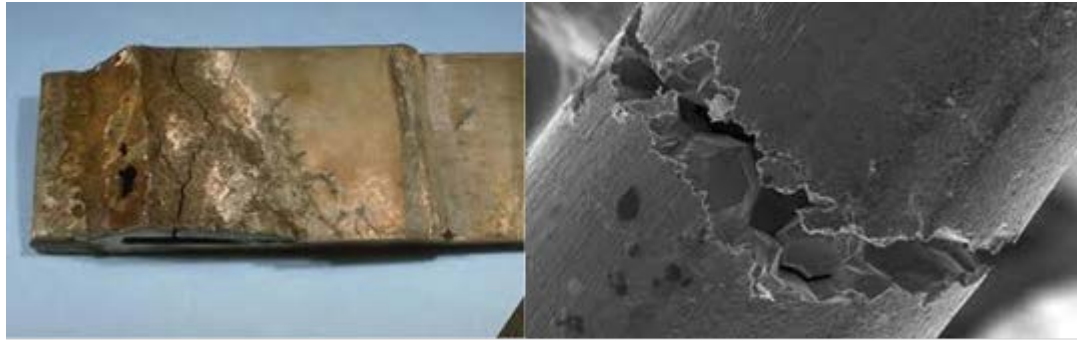


Figure 5 Stress corrosion (Kopeliovich, 2009)

-Erosion corrosion is the combination of erosion and corrosion, resulting in an increased rate at which the metal is lost.



Figure 6 Erosion corrosion (Kopeliovich, 2009)

The varying properties of different metals determine the means through which they corrode. Understanding the manner in which corrosion takes place can be used to determine the best metal for a given application and how to protect each from corrosion through the use of coatings, inhibitors, design, etc. The conditions metals are exposed to, such as: temperature, chloride level, sulfur level, precipitation, or time of wetness play a significant role in the amount of corrosion and the manner the corrosion occurs.

The manner in which these factors influence corrosion is as follows. An increase in temperature at constant relative humidity causes an increased rate of electrochemical reactions and therefore increasing the corrosion rate. However, when temperature is increased and the relative humidity generally decreases, there will cause evaporation and a decreased time of wetness. The time of wetness of the metal surface is closely related to the length of time the electrochemical reactions take place. The longer the time of wetness, the greater the length of time the corrosion has to take place. This makes clear that temperature, relative humidity, and time of wetness are closely related to the corrosion process. Moreover, precipitation also affects corrosion and time of wetness. Along with increasing the time of wetness the additional precipitation can affect the chloride/pollutant levels (sometimes adding to these levels but other times washing away these deposits).

2. Effect of deicer corrosion on metals

Though there are many pollutants, chemicals, etc. in the atmosphere that affect corrosion, the focus is on chlorides and NaCl due to their frequency in deicers. However, others will be covered as well. In general, the greater the concentration of chlorides the greater the corrosion rate, due to an increased electrolyte density on the surface of the metal and their role in electrochemical reactions. Sulfur dioxide (SO_2), pollutant produced when fossil fuels containing sulfur are combusted, has also been found to influence corrosion. Sulfur dioxide deposits on the surface of metals often form sulfuric acid in the presence of water. In some cases the addition of sulfuric acid at the electrolyte can increase corrosion. When oxidized, sulfur dioxide produces sulfate ions. The oxidization of sulfur dioxide is especially harmful to iron due to the formation of an autocatalytic attack. Some additional relatively common pollutants associated with manufacturing that have been found to increase corrosion rates are chlorine (Cl), hydrogen chloride (HCl), and hydrogen sulfide (H_2S). Lastly nitrogen compounds (NO_x) produced from combustion and solid matters in the atmosphere have also been found to accelerate the rate of corrosion (**Tullmin and Roberge, 2000a**). Suspended solid particulate matter (SPM) made up of sand, salt, and carbon particles can also contribute to atmospheric corrosion (**Ahmad et al., 2000a**).

The chapters below are some detail information of metals that are highly sensitive to corrosion. In general, they had been defined as the most used and corroded metals that had been found so far. However, there are more metals waiting for us to explore how well they resist to corrosion.

Steel:

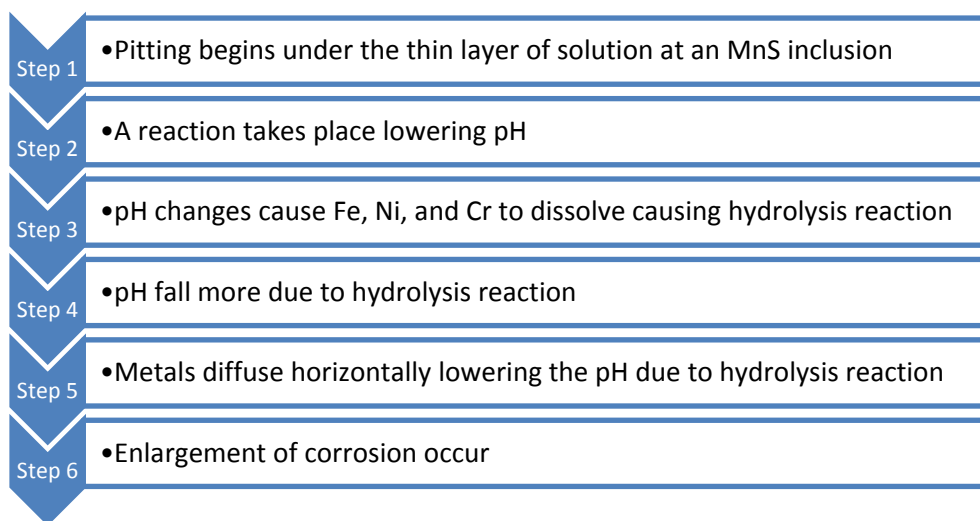
Uses:	Building materials, ships, automobiles
Elements might contain:	Iron, carbon, manganese, chromium and vanadium
Popularity:	Most commonly used

Steel is a kind of alloy containing iron, carbon, and other elements, which has been extensively used in industry, such as buildings, ships, automobiles, etc. Steel is mainly composed of iron followed by carbon, which generally makes up about 0.1-2.1% of the alloy by weight. Additional elements can include: manganese, chromium, vanadium, tungsten, etc., depending on the desired properties of the final steel product. The exposure of mild steel to a droplet containing salts leads to the formation of many small droplets around the initial droplet, and cathodic reaction take place in these wet areas, producing alkaline solutions that increase the pH and the rate of corrosion. However, sometimes when water transfer to these high pH and high alkaline locations, it will dilute the alkaline solution and decrease the pH, which can hinder the spread of corrosion (**Tsuru et al., 2004a**).

An example of how corrosion has affected certain type of steels is given as follows: The corrosion of Type 430 and 304 stainless steel could be observed when they are exposed to various sized droplets of MgCl_2 . It was found that as droplet diameter and thickness increased, probability of pitting corrosion and the pit diameter would increase as well (**Hastuty et al., 2010a**); (**Tsutsumi et al., 2007a**). Corrosion of those steels begins with the solution over the pitted areas becoming saturated with corrosion product causing decreased rates of corrosion near the center of the pit. The pitting corrosion then proceeds at the greatest rate near the perimeter of the droplet where corrosion product concentration is lowest, therefore causing corrosion in the lateral direction (**Hastuty et al., 2010a**)(**Tsutsumi et al., 2007a**). This lateral corrosion occurs because at the perimeter the metal ions

are not saturated and the perimeter is closer to the cathode, causing the metal dissolution to occur at a greater rate (Tsutsumi et al., 2007a)

Stainless steel (SS430 and SS304) were subjected to cyclic corrosion testing consisting of 1 hr immersion in chloride containing solution and 7 hr drying. It was found that pitting corrosion began during the dry cycle when a sufficient chloride concentration was obtained (Vera Cruz et al., 1997a). Another study on stainless steel with 1 hr immersion in chloride containing solution and 5 hr drying found that pit formation and growth occurs just before the surface of the metal dries completely (Vera Cruz et al., 1996a). During the drying stage, the surface dries causing passivation of the pit. As the pit grew the corrosion potential moved to less noble value. (Vera Cruz et al., 1997a; Vera Cruz et al., 1996a).



Scheme 1 **Mechanism for corrosion of type 305 stainless steel**

Pit formation and growth can also contributed by thin electrolyte layers that exist during atmospheric corrosion and causes a buildup of aggressive corrosion products over the anodic areas of the metal. The buildup of corrosion products is due to a lack of diffusion laterally; this lack of diffusion also causes pits to form in clusters (Vera Cruz et al., 1997a). Another study focusing on the corrosion of 304 SS under a thin layer of chloride solution found the active site of the pit grows in the horizontal direction and to a maximum depth of 10 μm . This pit morphology is contradictory to the results of the cyclic test mentioned earlier and under bulk chloride solutions, under these conditions deep pits form. A study found that the early corrosion of high strength steels is characterized by the formation of a layer of corrosion product, which is followed by preferential attack of the ferritic phase. Analysis of corrosion rate displayed that as pit depth increased the rate of corrosion decreased (Sanchez et al., 2008a). Pit growth occurs where the H^+ ions formed during hydrolysis diffuse. The only direction available for diffusion is the horizontal due to the thin film thickness. It was also found that the critical chloride concentration to be 5.8 M at a drying rate of 5.8% RH/h (Tsutsumi et al., 2005a).

As industrial technology improves, atmospheric corrosion is becoming more popular due to an increase of pollutants released into the atmosphere. Atmospheric corrosion products of steel are dependent on the composition of chemicals in the atmosphere at the specific location of the steel. Two chemicals found in the atmosphere that are influential on the rate of corrosion of metals are chloride ions and sulfate ions. Precipitation washes chloride ions away with ease, yet has little effect on the sulfate ion concentration. Therefore the chloride ion concentration at a given location depends

on the precipitation patterns while the sulfate ion concentration is relatively stable. The water absorption by the corrosion products is significant because it can be used to determine when corrosion is taking place at the interface between the metal and the corrosion products. In rural locations, the absorption of water undergoes a monomolecular model, which is much slower than the polymolecular model usually taking place in coastal location because of high chloride content. The greater water uptake rate causes a greater corrosion rate (**Corvo et al., 1996a**).

Recent researchers had discovered that on carbon steel surfaces, an anodic area forms at the location of NaCl and a cathodic region forms around it. The size of the cathodic region is proportional to the amount of NaCl coverage (**Nazarov and Thierry, 2004a**). Like the corrosion of many metals, it has been found that higher concentrations of chloride ion and sulfur cause higher corrosion rates of carbon steel. Furthermore it was found that the time of wetness had a greater impact on corrosion when the temperature was less than 25°C. Testing also found that in rural locations the main corrosion product was lepidocrocite (γ -FeOOH) and in coastal locations goethite (α -FeOOH) (**Mendoza and Corvo, 1999a**).

When carbon steel exposed to sulfur dioxide and sodium chloride in atmosphere, it will initially results in blisters on the metal surface at anodic sites. The blisters covers were composed of high amounts of iron chlorides and within the blisters were iron oxyhydroxides, oxides, sulfates, and hydroxides. Over time chloride demands for inward transport through the rust layer grows, resulting in decreased iron chloride formation. The disparity between the corrosion caused by sulfur dioxide and sodium chloride is that the formation of iron sulfates on the surface of the metal from sulfur dioxide does not decrease over time due to the acid regeneration mechanism. The sulfate associated corrosion is therefore influenced less by supply (**Allam et al., 1991**). The initial attack of the chloride ions causes more corrosion to occur than sulfate ions, but the sulfate ions undergo a more prolonged-consistent attack.

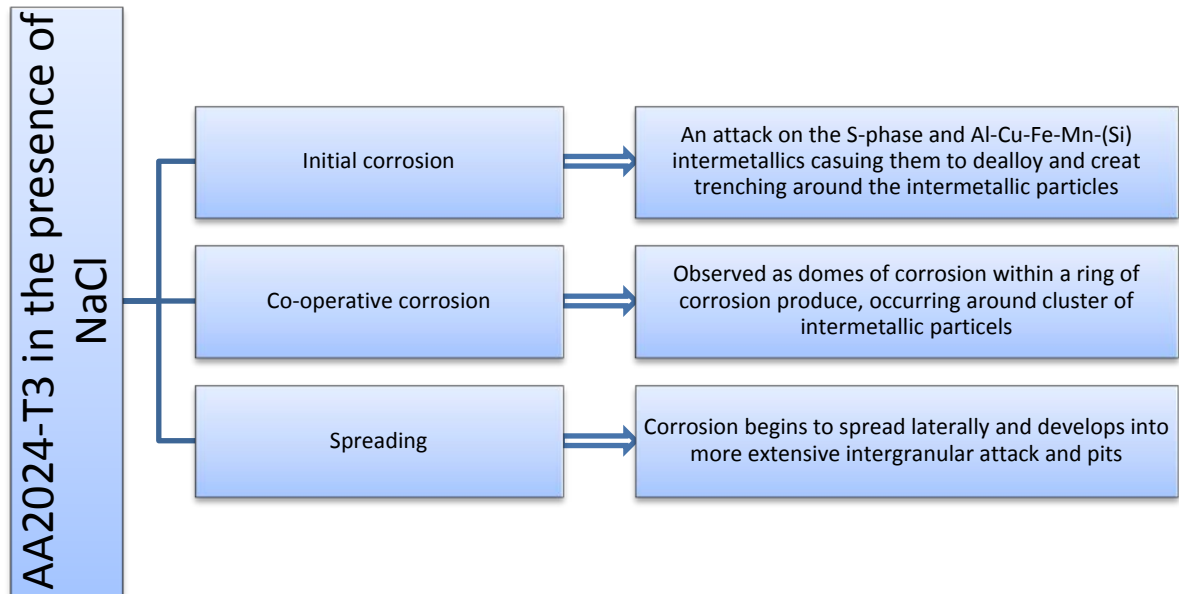
The influence of the nickel content in carbon steel on its corrosion in conditions of alternating 1 h immersion in 0.05M NaCl solution and 7 h drying stage at 60% RH and 25°C was monitored. The corrosion rates of the traditional carbon steel and carbon steel with 2.5% Ni were substantially increased by exposure to the cyclic testing. Carbon steels containing 5% Ni or greater had much lower corrosion rates. Analysis of the corrosion displayed that during the beginning of the drying period which caused the chloride concentration to increase, the corrosion rate grew and the corrosion potential values turned negative. The corrosion potential remains constant and sudden growth of the corrosion rate occurs midway through the drying process. This occurs due to a thinning of the electrolyte film on the surface allowing increased rate of O₂ transport. The O₂ transport rate controls the rate of corrosion because of the cathodic oxygen reduction reaction's dependence on the concentration of oxygen. The anodic, metal dissolution process also increases in this period. When the surface of the metal is almost dry the corrosion rate reduces due to inhibition of the anodic process caused by a lack of thin electrolyte film (**Nishikata et al., 1995a**). Similarly, coastal weathering steel was developed for locations with airborne chloride deposition rates of 0.05 mg/dm²/day. Modification of the steel involved removal of Cr because of its negative effects in the presence of chloride and the increase of Ni concentration by 3% causing a protective rust layer to form on the surface. The increase in Ni content has two benefits: first, the greater Ni content of steel decreases corrosion rate, and second, the protective rust layer production is due to the enrichment of Ni at the inner layer of the rust. Over the test period of 9 years it was found that metal loss due to corrosion was 0.15mm, which was about 10% of the value obtained for regular weathering steel (**Itou et al., 2000a**).

Aluminum (Al) and Aluminum Alloys:

Uses:	Automobiles, aircraft, packaging, construction and electronics
Elements might contain:	Copper, manganese, magnesium, silicon and zinc
Popularity:	Second to steel

Aluminum and aluminum alloys are used extensively in automobiles, aircraft, packaging, construction, electronics, and many more areas. Aluminum is one of the most commonly used metals, second only to iron. Aluminum alloys consist of aluminum and various amounts of the following elements: copper, manganese, magnesium, silicon, and zinc. Desirable characteristics of pure aluminum are its corrosion resistance and low density. Pure aluminum undergoes passivation, the formation of an oxide or nitride layer on the surface of the metal, which prevents additional corrosion. Aluminum alloys have been developed to improve the castability, strength, and other metallurgical properties depending on the desired application. High strength to weight ratio alloys have been developed for structural application in the aerospace and vehicle industries.

Aluminum alloy (AA2024-T3) in the presence of NaCl undergoes the following stages shown in Scheme 3:



Scheme 3 Aluminum alloy corrosion stage

Note: Intermetallic zones are inhomogeneous, different compositions have been found within the same intermetallic (**Queiroz et al., 2008a**).

Initial corrosion consisted of an attack on the S-phase and Al-Cu-Fe-Mn-(Si) intermetallics (**Queiroz et al., 2008a**) causing them to dealloy and create trenching around the intermetallic particles (**Hughes et al., 2011a**). The co-operative corrosion stage is observed as domes of corrosion within a ring of corrosion product, occurring around clusters of intermetallic particles (**Hughes et al.,**

2011b). After the prior penetrating attack of the grain boundary network, the corrosion begins to spread laterally. The minor grain attack then develops into more extensive intergranular attack and grain etchout, forming pits (**Hughes et al., 2011c**). For pure aluminum the portion of the metal located within the NaCl covered region is cathodic and the anodic attack occurs at the border with the adjacent passive metal (**Nazarov and Thierry, 2004a**).

When bare aluminum alloy 1050 (99.5% pure Al) is exposed to chlorides, the aluminum is passive and displays no localized corrosion at low chloride concentration. At a chloride concentration of 10 mg/m²d, after 2+ years of exposure spotting, blisters and pits were observed. When tested at a concentration of 50 mg Cl⁻/mg²d and greater, more extreme pitting corrosion was observed (**Gonzales et al., 2002a**) (Also has info on coating/anodizing protection). This makes clear that chloride concentration has a strong impact on the rate of corrosion, as chloride concentration increases so does the rate of corrosion and the extent of damage.

The corrosion of aluminum alloy LY12 exposed to cyclic accelerated corrosion tests in solutions of NaCl and NaHSO₃ was examined. Pitting corrosion was common with exposure to the NaCl, NaHSO₃, and NaCl + NaHSO₃ solutions. LY12 was selectively attacked and dissolved causing copper content at the surface to increase. Exposure to NaHSO₃ caused sulphate aluminum formation. When in contact with the NaCl + NaHSO₃ solution, corrosion began with pitting and corrosion product layer formation of sulphate aluminum formation. Corrosion continued with more extensive pitting and dehydration caused cracking. The combination of NaCl + NaHSO₃ exhibit cooperative corrosion causing extensive pitting and damage to the oxidation film, both of which result in an increased rate of corrosion (**Zhen-yao et al., 2007a**).

Aluminum exposed to cyclic wet-dry cycles of atmospheric corrosion was also found to have an increasing corrosion rate that eventually tapered off and remained constant. The degree of corrosion was strongly influenced by the time of wetness, temperature, and the angle at which the sample was positioned. The greater the time of the wetness, the higher the temperature, and the closer to horizontal the sample is oriented, the greater the rate of corrosion (**El-Mahdy and Kim, 2004a**).

Study had found that when aluminum alloys 2024 and 7075 exposed to coastal, industrial, and urban atmospheric corrosion. They had avoided pitting in the three atmospheric corrosion environments for the 20-year test period and held their mechanical properties due to the improved corrosion protection associated with the Mg in the cladding. The extruded samples performed less desirably, exhibiting exfoliation corrosion in the coastal and industrial environments, with 2024 affected by severe exfoliation corrosion in the coastal environment. It was also found that the extruded samples with exfoliation corrosion had declined mechanical properties proportional to the extent of exfoliation corrosion. No serious damage to the mechanical properties was observed for either of the extruded alloys in the dry urban environment (**Sun et al., 2009a**). Another manufacturing process, high temperature annealing, was found to make aluminum alloys 8006 and 3005 more vulnerable to filiform corrosion. This increase in vulnerability is caused by the formation of a reactive surface layer. The surface layer is likely more reactive due to one or more of the following elements: Mn, Fe, or Mg. The use of etching or anodizing to remove just 1 µm of metal from the surface was found to improve the filiform corrosion resistance. The process of cold rolling is an alternative to annealing, as it was not found to increase the likelihood of filiform corrosion (**Leth-Olsen and Nisancioglu, 1998a**).

It was found that the most corrosive environment was industrial, followed by coastal and urban, based on the test of weight loss, and the areas of corrosion were different in the different environments. For example, the samples were mounted at a 45° angle from horizontal, it was observed that the upward facing side experienced the most significant corrosion in the urban and industrial environments, yet in the coastal environment the backside did (**Sun et al., 2009a**). The reasoning for this is that in coastal areas chloride is the main chemical that causes corrosion but is easily washed away, while in urban and industrial areas the chemicals that cause corrosion adhere to the surface strongly and aren't as affected by precipitation. In coastal locations the backside avoids

precipitation/washing, allowing significant chloride concentrations to build and corrosion to take place.

Magnesium Alloys:

Uses:	aerospace industry, electronics, and sporting equipment
Elements might contain:	Fe, Ni, Cu, Co and Zr
Popularity:	famous in aerospace industry
Characters:	Low weight and high strength

Recently the use of magnesium alloys has grown significantly. Initial interest in magnesium alloys originated in the aerospace industry due to their low weight and high strength characteristics. The application of magnesium alloys has spread and they are now being used to produce electronics, automobiles, bicycles and sporting equipment. These alloys also have desirable castability and workability characteristics. Improved mechanical properties of magnesium have caused its growth in usage, yet a major issue that is still faced is overcoming their susceptibility to corrosion.

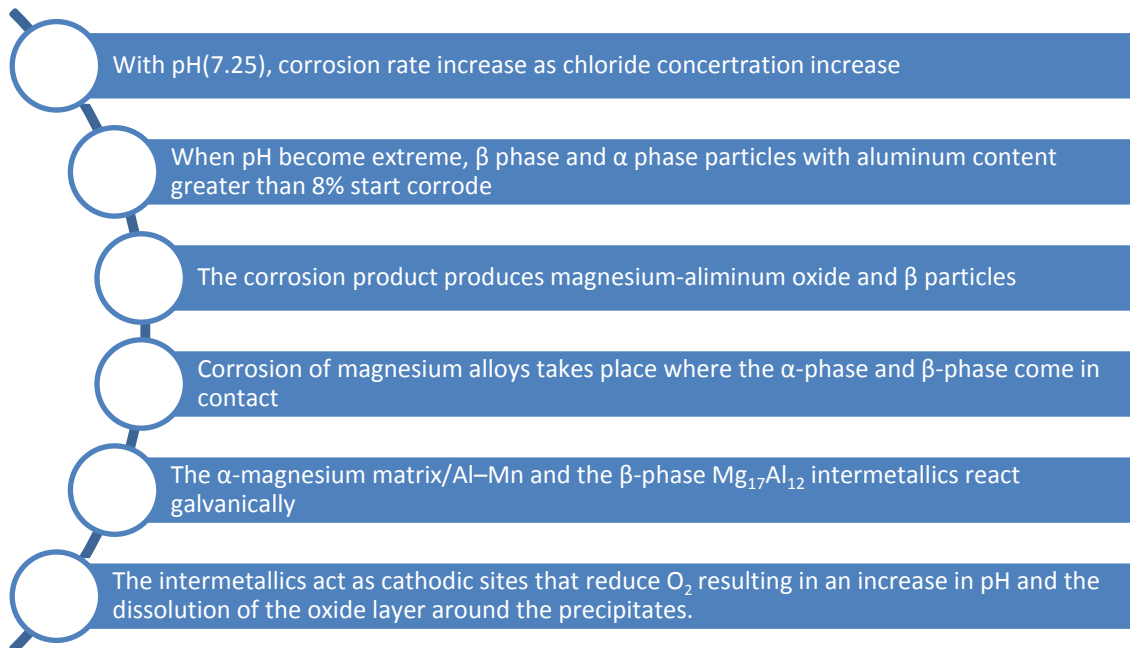
In terms of engineering materials, magnesium is extremely reactive. Due to the reactivity of magnesium, galvanic corrosion between magnesium and other metals it is affixed to is a major issue. In order to avoid galvanic corrosion, fasteners and insulation must be applied to these boundaries. Within the alloy itself, it is highly corrosive due to its tendency toward dissolution and the existence of impurities and different phases that partake in micro-galvanic corrosion. These characteristics make corrosion prevention extremely important. Magnesium exhibits the negative difference effect (NDE), rather than a decreasing potential like other metals exhibit, the hydrogen evolution rate increases as the potential increases. It has been found that controlling the amount of each substituent in the magnesium alloys is extremely important in order to limit substituents that may increase corrosion rates. The components Fe, Ni, Cu, and Co at concentrations of 0.2% of the alloy or less were found to accelerate corrosion rate drastically in the presence of salt water. The components Ag, Ca, and Zn were found to increase corrosion rates moderately at concentrations of 0.5-5%. Lastly Al, Sn, Cd, Mn, Si, and Na had almost no effect on the corrosion rate at concentrations up to 5%. These concentrations are known as tolerance limits and depending on the concentrations of these substituents, the limits can be used to gauge the rate at which corrosion will occur.

There are two main types of Magnesium alloys, those containing Zr and those without. Those without Zr are known as Zr-free alloys and usually contain Al. The corrosion of Zr-free alloys is related to the amount of Fe, Ni, Cu, and Co present in the alloy. These elements are impurities, the fewer impurities or the purer the metal, the lower the corrosion rate. On the other hand, Zr is used in alloying because it refines grains and can be alloyed with Re, Th, and Ag to create alloys with high performance properties. The Zr-containing alloys are generally pure and have similar corrosion resistances as pure Mg or high-purity Zr-free alloys. The elements Fe, Ni, Cu, and Co react with Zr and are removed, which will lead to the previously mentioned high purity of the alloys (**Song and Atrens, 2005a**).

When a semi-protective film covers the surface of magnesium, general corrosion does [not](#) occur, but localized corrosion is an issue, and a sample will be impurities act as cathodes and cause micro-galvanic corrosion. The most common improvements for protective film are removal of

impurities, and/or passivation of impurities which will increase corrosion resistance. (Song and Atrens, 2004a).

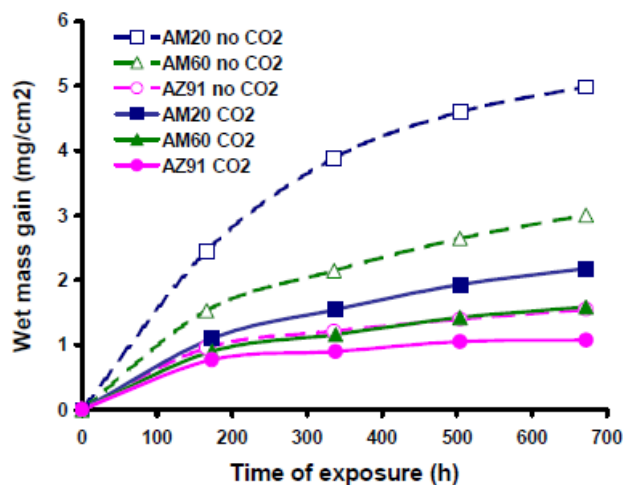
When focusing on the effect of chloride concentration on ingot and die-cast magnesium corrosion, corrosion undergoes the following steps as shown in Scheme 4.



Scheme 4. Magnesium Alloys corrosion steps.

It was found that at near neutral pH (7.25) the corrosion rate for both increased as the chloride concentration increased. At raised chloride concentration and extremes in pH, the normally stable β phase particles and α phase particles with aluminum content greater than 8% were corroded. The corrosion product was composed of magnesium-aluminum oxide and β particles (Ambat et al., 2000a). Corrosion of magnesium alloys takes place where the α -phase and β -phase come in contact. The α -magnesium matrix/Al-Mn and the β -phase $Mg_{17}Al_{12}$ intermetallics react galvanically (Pardo

et al., 2008a). The intermetallics act as cathodic sites that reduce O_2 resulting in an increase in pH and the dissolution of the oxide layer around the precipitates, after which the adjacent matrix is attacked (Arenas et al., 2001a). Micro-galvanic corrosion takes place when matrix has a lower corrosion potential than the second phases causing the magnesium to react with the less corrosive metal. It takes place in the same manner, magnesium in contact with a less reactive metal, just on a larger scale (Song and Atrens, 2004a). For example, macro-galvanic corrosion can occur between the magnesium alloy



and a

Figure 7 (Lindstrom et al., 2003a)

structural metal it is attached to. Magnesium alloy

AZ91D was subjected to atmospheric corrosion of the following types: urban, rural and marine. Corrosion begins at the α -phase in grains between the α -phase and the eutectic α/β -phase. The α -phase acts as the anode and the eutectic α/β -phase act as the cathode. The most common corrosion product formed at all three of the test locations was found to be magnesium carbonate hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), which delivered negligible protection. The variation in environment can influence the corrosion rate. For example, in the marine conditions the rate was $4.2 \mu\text{m}/\text{year}$ and in the rural conditions the rate was $2.2 \mu\text{m}/\text{year}$ (Jonsson et al., 2008a).

When Magnesium alloy exposed to 95% RH with surface concentration of $70 \mu\text{g}/\text{cm}^2$ NaCl, the corrosion begins at locations with high concentrations of NaCl and forms magnesite (MgCO_3). Much of the magnesite (MgCO_3) formed turns into nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) after a couple of days. The corrosion products are therefore magnesium carbonate hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$). Furthermore, prolonged exposure led to the development of pits, and hydromagnesite crusts were found within the pits. These crusts prevent the transfer of O_2 and CO_2 to the surface of the alloy, causing brucite ($\text{Mg}(\text{OH})_2$) to be formed (Jonsson et al., 2007a). Researchers also found that when the amount of CO_2 reaches certain level, it will impact the corrosion of magnesium alloys in the presence of NaCl (shown in Figure 7). For example, when magnesium alloys AM20, AM60, and AZ91 were tested in the presence of CO_2 , general corrosion was observed on the surfaces of the metals, producing a corrosion product layer of $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (Lindstrom et al., 2003a; Lindstrom et al., 2002a).

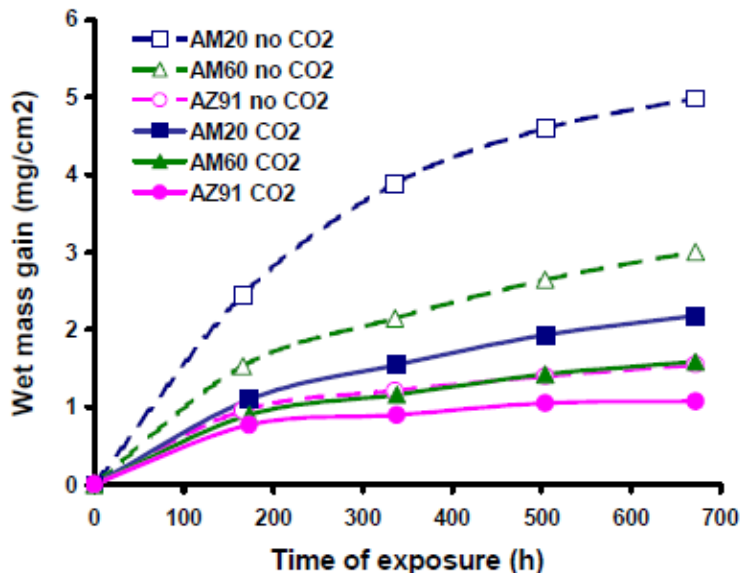


Figure 8 Wet mass gain vs. exposure time for magnesium alloys samples exposed at 22°C . The RH was 95% and the amount of NaCl was $70 \mu\text{g}/\text{cm}^2$ NaCl. The CO_2 concentrations was $<1 \text{ ppm}$ and 350 ppm CO_2 , respectively. (Lindstrom et al., 2003a)

significant in order to understand corrosion in locations with varying carbon dioxide concentrations. For example, the testing with carbon dioxide present is similar to on-vehicle exposure, while the testing in the absence of carbon dioxide is similar to corrosion within cracks or under solution.

In order to improve the corrosion resistance of magnesium alloys research has been conducted to optimize their resistance. It has been found that greater aluminum concentrations in the alloy had reduced the corrosion rate of the pure Mg in the presence of NaCl (Pardo et al., 2008a).

was found to inhibit the corrosion of the magnesium alloys. This inhibition is attributed to the fact that the presence of greater CO_2 concentration lowers the pH of the electrolyte layer, leads to a more stabilized passive film, and produces the corrosion product which inhibits corrosion (Lindstrom et al., 2003a). Without CO_2 present significant pitting occurs and the corrosion product, $\text{Mg}(\text{OH})_2$, is produced. In an environment lacking CO_2 , corrosion occurs four times faster than in the presence of CO_2 and is likely due to the corrosion product, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, providing limited corrosion protection (Lindstrom et al., 2002a).

This information is

For Magnesium-Aluminum alloys, research has found that the β -phase ($Mg_{17}Al_{12}$) location and prevalence influence the corrosion resistance. Large amounts of β -phase ($Mg_{17}Al_{12}$) create an anodic barrier and reduce the corrosion rate of the α -phase, while small amounts create cathodes that increase the corrosion rate (**Pardo et al., 2008a**). The manner in which the magnesium alloy is shaped has also been found to influence its corrosion resistance. A study on AZ91 alloy found that when extruded; the alloy had less corrosion resistance than when cast. This occurs because extrusion increases the dislocation density, twins, and grain boundaries. Extrusion also changes the positioning of the β phase, after extrusion the β phase acts mainly as a galvanic cathode and increases the corrosion rate. While the β phase in cast alloy for is in a net shape that acts as a corrosion barrier or as the aforementioned galvanic cathode (**Zhang et al., 2011a**).

Additional studies performed have found significant variation in the corrosion rates observed in field tests versus salt immersion and salt spray tests. Tests have shown that corrosion rates in the field are slowed due to the formation of a protective corrosion product; yet salt immersion and salt spray tests have shown no decrease in corrosion rate (**Lindstrom et al., 2003a**).

Zinc (Zn):

Uses:	Anti-corrosive coating, hot dipping
Elements might contain:	N/A
Popularity:	Famous in electrochemical process
Characteristics:	Acts as sacrificial coating

Zinc is commonly used as an anti-corrosive coating for iron and steel and it is often applied through hot dipping or electrochemical processes. It is more reactive than the other metals and therefore it is always used as a sacrificial coating layer. The corrosion mechanism of zinc in a sodium chloride containing environment is as follows, the deposition of an initial droplet containing NaCl on the surface of the zinc is followed by the dispersion of an alkaline electrolyte film that extends from it, doubling or tripling the initial radius of the drop. The corrosion product found in the center of the initial droplet is zinc hydroxychloride and at the perimeters is sodium carbonate (Na_2CO_3). The rate of corrosion dispersion is related to the electrical potential gradient between the anodic region at the center of the initial droplet and the cathodic region at the perimeter (**Neufeld et al., 2002a; Nazarov and Thierry, 2004a**).

Even with the significant prevalence of sulfur in environments where vehicles operate, few tests looking at the effects of how sulfur impact on zinc have been taken. The results for those experiments showed that when additional presence of sulfur added, it had caused the corrosion product, sodium zinc hydroxychloride sulfate ($ZnSO_4 \cdot 3Zn(OH)_2 \cdot NaCl \cdot xH_2O$), to be formed on the zinc surface, and sodium zinc hydroxychloride sulfate was found to have an inhibiting effect (**Svensson and Johansson, 1993a**).

Another research focused on the corrosion of zinc in the presence of the following chloride salts and sulfates: NaCl, NH_4Cl , $ZnCl_2$, $MgCl_2$, Na_2SO_4 , $(NH_4)_2SO_4$, $ZnSO_4$, and $MgSO_4$, had been tested. It has been proved that cation is the most influential factor on the rate of corrosion, with the sodium ion found to be most corrosive of the cations tested. It also been found that corrosion rate of zinc was correlate directly with the amount of sodium ion present, whether the sodium ion was bonded to a chloride salt or a sulfate made no difference. This finding questions the common method of relating corrosion to the chloride concentration, and suggests that relating corrosion to amount of sodium ion present may be more accurate (**Lindstrom et al., 2002a**).

Cast Iron:

Uses:	Automotive industry, bridges, textile mills
Elements might contain:	Carbon, Silicon, Nickel, Chromium
Popularity:	Parts for automobile
Characteristics:	Brittle, Solidifies at a lower temperature

There was a notice (on a poster) in a corrosion exhibition in Brussels (1937):

"While you read this
760 kg iron
has been corroded!"

Even the usage of cast iron has become less demanded today compare to 1937 due to the improvement of technology with new materials discovered, the cost of cast iron (seen from Figure 8) caused by corrosion is still leading a notable portion in the economy growth, especially when it is the major material for automobile parts such as cylinder heads (declining usage), cylinder blocks and gearbox cases (declining usage).



Recently, testing on the atmospheric corrosion of cast iron in the presence of chloride and sulphur containing pollutants was performed by Xia's group (**Xia and Chunchun, 2006a**). They found iron corrosion takes place via the "acid regeneration cycle mechanism" when exposed to either chloride or sulphite. When HSO_3^- is present, the initial corrosion is greater than in the presence of Cl^- because of HSO_3^- causes pitting corrosion and has a greater level of surface activity. As well as the greater level of surface activity, SO_2 is produced by the corrosion reaction and can substitute for oxygen acting as a depolarizer. The corrosion process included anodic dissolution and formation of the corrosion products: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 9\text{H}_2\text{O}$ and $\gamma\text{-FeOOH}$; none of which provide significant corrosion protection. As the rust layer compacted and thickened, corrosion protection increased.

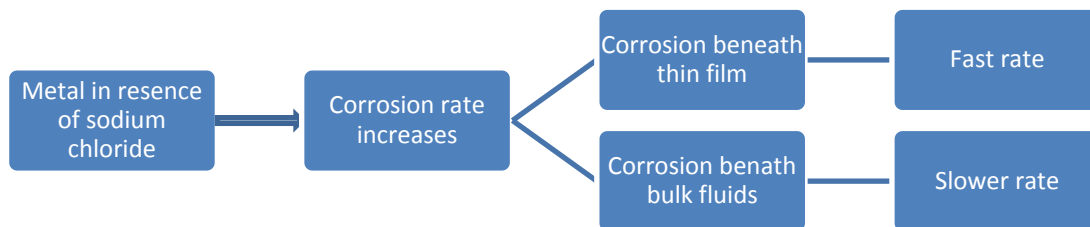
During initial stages of corrosion when both HSO_3^- and Cl^- are present on cast iron, the corrosion rate is slower than corrosion that occurs in the presence of just HSO_3^- due to competitive absorption, but after extensive periods of exposure the combination of HSO_3^- and Cl^- will cause greater damage than HSO_3^- alone. The combination of auto-catalysis and mobility/penetration effects of Cl^- was found cause cracks and flaws. In the presence of Cl^- , the rust layer conversion from $\gamma\text{-FeOOH}$ to $\alpha\text{-FeOOH}$ was inhibited, reducing the protection provided by the layer (**Xia and Chunchun, 2006a**).

Total immersion test and potentiostatic polarization curves have been used to test the changes with time in the corrosion rate and corrosion current density on a cast iron electrode in various aqueous salt solutions. It has been found the initial rate of corrosion is high for NaCl and KCl and the relative increase in corrosion rate is less as the reaction proceeds, because there remains no direct contact between metal surface and corrosive ions by corrosion product and excess of cations nearby the metal surface. On the other hand in the KBr and KI test solutions the initial corrosion rate is less due to non-availability of anions at the metal surface. After initiation of reaction, the rate increases continuously and is not hindered by corrosion as in the case of KCl, NaCl and CaCl_2 . The negative increase in CaCO_3 and less increase in NaHCO_3 of corrosion rate indicates the non-corrosive behavior of CaCO_3 and NaHCO_3 because of less mobility of Ca^{2+} and HCO_3^- ions (Chandra et al 1994; Hammout et al 1995).

Few other studies have examined the role of different temperatures in distribution system cast iron corrosion. In general, studies of distribution systems found the manifestations of corrosion to be less severe in colder winter months. Also, one laboratory study found decreased weight loss for iron samples held at 13 °C versus 20 °C. (Fiksdal and L. Water, 1995)

General Corrosion and Deicer Information:

The basic corrosion mechanism is given as Scheme 5. It has been found that the film thicknesses on the order of micrometers displays the greatest rates of corrosion because cathodic reaction rate is dependent on the rate at which oxygen can diffuse through the film from the air to the metal. The greater the film thickness the slower the diffusion and the reaction. (Dubuisson et al., 2007a). For example, a test of film thickness on AA2024-T3 found corrosion to occur at its greatest rate when the thickness of the film is between 105-170 μm depending on how long the corrosion had been taking place (Cheng et al., 2004a).



Scheme 5 Basic Corrosion Mechanism

Sodium chloride causes the formation of a thin electrolyte film because it draws water from vapor in the air (Dubuisson et al., 2007a).

In cyclic humid conditions where wet-dry-wet periods occur, it was found that MgCl_2 caused more corrosion damage than NaCl did to vehicles. However, when metals were exposed to by dry and an immersion condition, NaCl was more corrosive. These results are attributed to greater viscosity of MgCl_2 relative to NaCl, allowing it to adhere to the metal better and form crystallize on the surface in the cyclic conditions (Lazarus, 2009a). Another study found that MgCl_2 was more corrosive than NaCl when tested using the cyclic exposure test SAE J2334. Additionally, when the continuous spray

test using ASTM B117, it was found that NaCl was more corrosive than MgCl₂ (Xi and Xie, 2002a). These studies show how great of an impact the environment/conditions in which the deicers are used.

Besides the impact of NaCl and MgCl₂, studies found that the effect of CO₂ concentration in the presence of NaCl on corrosion of copper also have a large influence on the secondary spreading of the NaCl containing electrolyte. The low CO₂ concentration (5 ppm) resulted in a much greater area covered by secondary spreading than was seen at the high CO₂ concentration (350 ppm). The cathodic areas therefore covered by the secondary spreading experienced higher rates of corrosion. These results are important to understanding corrosion in locations where CO₂ concentrations are low, such as under films and deposits (Chen et al., 2005a).

Examination of aluminum alloy 2519 samples for their susceptibility to stress-corrosion cracking (SCC) found in unstressed samples passed the standard SCC tests. But after exposure to chlorides and stress, the samples failed the standard SCC tests. Stress assisted pitting due to exposure to stress and saline rich conditions greatly reduced the load-bearing strength of the AA 2519 samples (Kramer et al., 2002a). Special attention must be given to ensure that the metals used in each application meet their requirements both before and just as importantly, after exposure to corrosive environments and stress.

Microbially Induced Corrosion:

An alternative to deicer-induced corrosion is that caused by microbes. Focus on understanding microbially induced corrosion has grown significantly in recent years. If not properly managed, microbially influenced corrosion (MIC) may have significant economic or safety consequences for a wide range of industries. Microbes can actively participate in the corrosion processes and affect their thermodynamics and kinetics, interfere with the electrochemical reactions at the anode, at the cathode, or both, and alter the metal/solution interface and the redox potential of the substratum via a host of often interrelated mechanisms. Over the last two to three decades, significant advancements have been made to improve the understanding of dynamic interactions between microbes and metallic surfaces, including the role of biofilm in MIC and associated alternations at the metal/solution interface (Shi et al, 2011). There is now a growing amount of information related to the mitigation of MIC, including technological advances in identifying microbes and detecting and characterizing MIC; chemical or biological approaches to sterilize the system (e.g., with fumigants, biocides, or biophages) or remove biofilms, to inhibit the growth and/or metabolism of corrosion-related microbes, and to prevent or reduce the formation of biofilms; surface treatments (anti-microbial or antifouling coatings and superhydrophobic surfaces); and beneficial use of live biofilms or microbial EPS (Shi et al, 2011) So complete understanding MIC and its application is a key to corrosion prevention.

3. Conclusions

In this chapter, we discussed some fundamental knowledge about deicer corrosion effects on metals. Metals act differently to corrosion base on their unique character and molecule structure. For example, the corrosion level of aluminum and magnesium is different at same NaCl concentration because aluminum is more active than magnesium in natural form as an anode. Deicer corrosion is also affected by the concentration of corrosive chemicals such as NaCl, HCl, H₂S, sulfur compounds, etc. An example is pure aluminum has no effect when exposed to low concentration of chloride but it starts pitting when the concentration of chloride rises to 10mg/m²d. On the other hand, the more exposed area to corrosive solution, the bigger corrosion will result. This chapter only illustrated few of many metals that showed those characters. In general, deicer corrosion is a common issue exists in our society.

References

- Ahmad, Z.; Allam, I.M.; Abdul Aleem, B.J. "Effect of environmental factors on the atmospheric corrosion of mild steel in aggressive sea coastal environment." *Anti-Corrosion Methods and Materials* 47 (2000) 215-225.
- Allam, I.M.; Arlow, J.S.; Saricimen, H. "Initial Stages of Atmospheric Corrosion Steel in the Arabian Gulf." *Corrosion Science* 32 (1991): 417-432.
- Arenas, M.A.; Bethencourt, M.; Botana, F.J.; de Damborenea, J.; Marcos, M. "Inhibition of 5083 aluminium alloy and galvanized steel by lanthanide salts." *Corrosion Science* 43 (2001): 157-170.
- Chen, Z.Y., Persson, D., Samie, F., Zakipour, S., Leygraf, C. "Effect of Carbon Dioxide on Sodium Chloride-Induced Atmospheric Corrosion of Copper." *Journal of the Electrochemical Society* 152 (2005): B502-B511.
- Corvo, F., Betancourt, N., Mendoza, A. "The Influence of Airborne Salinity on the Atmospheric Corrosion of Steel." *Corrosion Science* 37 (1995): 1889-1901.
- Dubuisson, E., Lavie, P., Dalard, F., Caire, J.P., Szunerits, S. "Corrosion of galvanized steel under and electrolytic drop." *Corrosion Science* 49 (2007): 910-919.
- El-Mahdy, A. and Kim, K.B. "AC impedance study on the atmospheric corrosion of aluminum under periodic wet-dry conditions." *Electrochimica Acta* 49 (2004): 1937-1948.
- Gonzalez, J.A., Morcillo, M., Escudero, E., Lopez, V., Otero, E. "Atmospheric corrosion of bare and anodized aluminium in a wide range of environmental conditions. Part I: Visual observations and gravimetric results." *Surface and Coatings Technology* 153 (2002): 225-234.
- Guthrie, J., Battat, B., Grethlein, C. "Accelerated Corrosion Testing." *The AMPTIAC Quarterly* 6.3 (2002): 11-15.
- Hastuty, S., Nishikata, A., Tsuru, T. "Pitting corrosion of Type 430 stainless steel under chloride solution droplet." *Corrosion Science* 52 (2010): 2035-2043.
- Hughes, A., Boag, A., Glenn, A.M., Muster, T.H., McCulloch, D., Ryan, C., Luo, C., Zhou, X., Thompson, G.E.. "Corrosion of AA2024-T3 Part II: Co-operative corrosion." *Corrosion Science* 53 (2011): 27-39.
- Itou, M., Tanabe, K., Ito, S., Kusunoki, T., Usami, A., Kihira, H., Tsuzuki, T., Tomita, Y. "Performances of Coastal Weathering Steel." *Nippon Steel Report* No. 81 January (2000): 79-84.
- Jones, D.A. *Principles and Prevention of Corrosion*. 2nd Ed. New Jersey: Prentice Hall, 1996.
- Jonsson, M., Persson, D., Leygraf, C. "Atmospheric corrosion of field-exposed magnesium alloy AZ91D." *Corrosion Science* 50 (2008): 1406-1413.
- Kramer, L.S., Blair, T.P., Blough, S.D., Fisher, J.J., Pickens, J.R. "Stress-Corrosion Cracking Susceptibility of Various Product Forms of Aluminum Alloy 2519." *Journal of Materials Engineering and Performance* 11 (2002): 645-650.

- Lazarus, J. "Maintenance and Corrosion of Fleet Equipment Due to MgCl_2 Use as a Deicer." ODOT Abbreviated Literature Review (2009): 1-8.
- Leth-Olsen, H. and Nisancioglu, K. "Filiform Corrosion of Aluminium Sheet. I. Corrosion Behaviour of Painted Material." Corrosion Science 40 (1998): 1179-1194.
- Lindstrom, R., Johansson, L.G., Svensson, J.E. "The Influence of NaCl and CO_2 on the Atmospheric Corrosion of Magnesium Alloy AZ91." Materials and Corrosion 54 (2003): 587-594.
- Lindstrom, R., Svensson, J.E., Johansson, L.G. "The Influence of Salt Deposits on the Atmospheric Corrosion of Zinc." Journal of the Electrochemical Society 149 (2002): B57-B64.
- Mendoza, A.R. and Corvo, F. "Outdoor and indoor atmospheric corrosion of carbon steel." Corrosion Science 41 (1999): 75-86.
- Morcillo, M., Chico, B., Mariaca, L., Otero, E. "Salinity in marine atmospheric corrosion: its dependence on wind regime existing in the site." Corrosion Science 42 (2000): 91-104.
- Nazarov, A. and Thierry, D. "Rate-determining reactions of atmospheric corrosion." Electrochimica Acta 49 (2004): 2717-2724.
- Neufeld, A.K., Cole, I.S., Bond, A.M., Furman, S.A. "The initiation mechanism of corrosion of zinc by sodium chloride particle deposition." Corrosion Science 44 (2002): 555-572.
- Nishikata, A., Yamashita, Y., Katayama, H., Tsuru, T., Usami, A., Tanabe, K., Mabuchi, H. "An Electrochemical Impedance Study on Atmospheric Corrosion of Steels in a Cyclic Wet-Dry Condition." Corrosion Science 37 (1995): 2059-2069.
- Pardo, A., Merino, M.C., Coy, A.E., Arrabal, R., Viejo, F., Matykina, E. "Corrosion behavior of magnesium/aluminum alloys in 3.5% wt NaCl." Corrosion Science 50 (2008): 823-834.
- Queiroz, M., Magnani, M., Costa, I., de Melo, H.G. "Investigation of the corrosion behavior of AA 2024-T3 in low concentrated chloride media." Corrosion Science 50 (2008): 2646-2657.
- Sanchez, J., Fullea, J., Andrade, C., Gaitero, J., Porro, A. "AFM study of early corrosion of a high strength steel in a diluted chloride solution." Corrosion Science 50 (2008): 1820-1824.
- Song, G. and Atrens, A. "Understanding the Corrosion of Magnesium Alloys." 16th International Corrosion Congress, September 19-24 (2005): 1-6.
- Sun, S., Zheng, Q., Li, D., Wen, J. "Long-term atmospheric corrosion behavior of aluminium alloys 2024 and 7075 in urban, coastal and industrial environments." Corrosion Science 51 (2009): 719-727.
- Svensson, J.E. and Johansson, L.G. "A Laboratory Study of the Initial Stages of the Atmospheric Corrosion of Zinc in the Presence of NaCl; Influence of SO_2 and NO_2 ." Corrosion Science 34 (1993): 721-740.
- Tsuru, T., Tamiya, K., Nishikata, A. "Formation and growth of micro-droplets during the initial stage of atmospheric corrosion." Electrochimica Acta 49 (2004): 2709-2715.

- Tsutsumi, Y., Nishikata, A., Tsuru, T. "Pitting corrosion mechanism of Type 304 stainless steel under a droplet of chloride solutions." *Corrosion Science* 49 (2007): 1394-1407.
- Tullmin, M. and Roberge, P.R. "Ch. 18 Atmospheric Corrosion." Uhlig's *Corrosion Handbook*, 2nd Edition (2000): 305-321.
- Vera Cruz, R.P., Nishikata, A., Tsuru, T. "AC Impedance Monitoring of Pitting Corrosion Stainless Steel Under a Wet-Dry Cyclic Condition in Chloride-Containing Environment." *Corrosion Science* 38 (1996): 1397-1406.
- Water Distribution Systems. Goteborg, Sweden, 111-115 (1995).
- Xi, Y. and Xie, Z. "Corrosion Effects of Magnesium Chloride and Sodium Chloride on Automobile Components." Colorado Department of Transportation Research Branch Report #CDOT-DTD-R-2002-4. (2002).
- Xia, C. and Chunchun, X. "Effect of chloride on the atmospheric corrosion of cast iron in sulphur-bearing pollutant environments." *Anti-Corrosion Methods and Materials* 53/3 (2006): 161-168.
- Zhang, T., Shao, Y., Meng, G., Cui, Z., Wang, F. "Corrosion of hot extrusion AZ91 magnesium alloy: I-relation between the microstructure and corrosion behavior." *Corrosion Science* 53 (2011): 1960-1968.
- Zhen-yao, W., Teng, M., Wei, H., Guo-cai, Y. "Corrosion behavior on aluminum alloy LY12 in simulated atmospheric corrosion process." *Trans. Nonferrous Met. Soc. China* 17 (2007): 326-334.
- Dmitri-Kopeliovich, http://www.substech.com/dokuwiki/doku.php?id=galvanic_corrosion&do=show, 2009/05/16

Chapter 3 Proactive Approaches to Corrosion Prevention

This chapter discusses proactive approaches to corrosion prevention, including materials selection, design improvements, and maintenance practices. First, a discussion of how material selection, including the methods and knowledge observed from past experiences, can be utilized for corrosion protection is presented. As discussed in the last chapter, different metals have various characteristics and the corrosion types associated with these metals greatly vary. Certain metals are more susceptible to corrosion, which makes choosing materials for desired designs an essential component of corrosion protection. Subsequently, information is presented on how to improve and maintain designs that will assist in the prevention of equipment corrosion. Finally, maintenance practices are discussed as a way to prevent equipment corrosion.

1. Materials Selection

For past decades, countless amounts of time and effort have been dedicated to anticorrosion research. Advancements in technology have allowed for various improvements in material selection to minimize corrosion. Furthermore, results from anticorrosion material research laboratories and other resources are constantly being evaluated in order to find the best materials for use in corrosive environments.

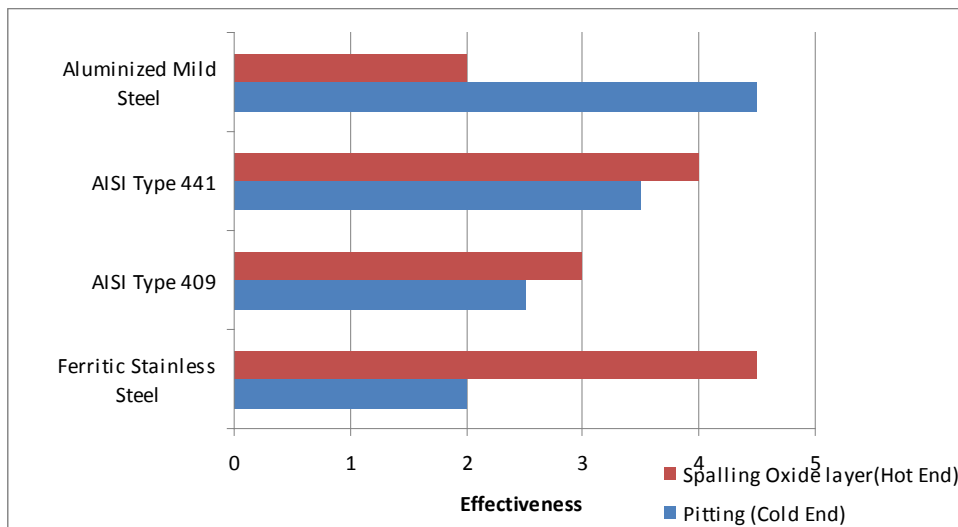


Figure 1. A study of exhaust systems exposed to de-icing salts. (Sephton, 2003)

Figure 1 shows an investigation of exhaust systems exposed to de-icing salts. Aluminum is one of the most widely used metals only behind steel. In natural environments unalloyed aluminum has superior corrosion resistance properties than carbon steel but has poor mechanical strength. Metallurgists and corrosion engineers are trying to improve the aluminum mechanical behavior without losing the corrosion resistance properties. One known exception is for marine applications when magnesium is added in the 5xxx series to balance strength and corrosion resistance. It is recommended to use exfoliation resistant tempers like T76 or 7xxx alloys with copper if a high-strength alloy is needed. Copper-free alloys and alloys with low noble impurities or alloying elements have high pitting corrosion resistance. Alloys in the 1xxx, 2xxx, 3xxx, 5xxx, and 6xxx series have the highest corrosion resistance properties. Corrosion resistance is optimum in environments with a pH range of 4 to 9. Out of this range the aluminum oxide film that forms on the metal surface and protects the metal degrades forming Al^{3+} ions in acidic conditions or AlO_2^- in alkaline conditions (Reboul and Baroux, 2011a).

Within the commercial aircraft industry, aluminum alloys, high strength-to-weight ratio alloys, are associated with the most corrosion problems due to the corrosion susceptible nature of aluminum alloys (**Adjorlolo and Marceau, 2005**).



Figure 2. Aircraft Corrosion

Corrosion needs to become a high priority during material selection. Many studies have shown that T-7 has high corrosion resistant properties with only a 10% decrease in strength compared to T-6 temper. A common alloy that has been used for several decades and is still used today in aircraft is Al 7075-T6, which is very vulnerable to corrosion. Alloys 7055-T7751, 7150-T7751 and 7050-T7651 have considerable better corrosion resistance and mechanical properties than 7075-T651 but have only recently been utilized.

A field study recently conducted by Uchida and Mochizuki found that the use of zinc coating on steel sheet had anticorrosion performance. A direct relationship between corrosion and the amount of zinc coating weight on steel sheets was also observed (**Uchida and Mochizuki 2000**).

2. Design Improvements

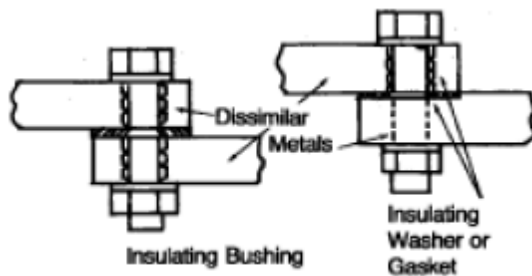
Corrosion prevention and control begins with material selection, however the use of corrosion engineering principles in design can have a significant impact. If an operating environment is considered to be corrosive, design engineering of components should reflect this situation. For example, a design should be used to avoid locations where water may accumulate. Heat treatment process called Retrogression Re-Aging (RRA) is another approach to improve the corrosion resistant properties of designs. RRA treatment consists of a retrogression phase of heating at 195 °C for up to 40 minutes, quenching, and then heating at 120 °C for 24 hours, the re-aging phase. RRA has been tested by the Air Force Research Laboratory and found it to be successful for improving corrosion resistance of 7075-T6 alloy (**Agarwala, 2004**).

Some general trends in corrosion engineering design have been found to greatly decrease the detrimental effect of corrosion. For example, time of wetness has a direct impact on corrosion of materials, so the design needs to be representative of this and allow for prevention of water collection through the use of drainage holes or positioning techniques.

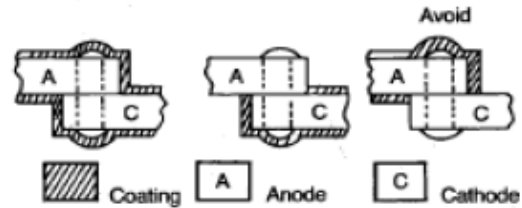
There are many tips of prevent corrosion in designs. For example, the use of more resistant alloys to decrease the tensile stress can be helpful in situations where stress corrosion cracking dominates. Properly designed welded joint and gaskets should be utilized to minimize crevice corrosion. Contact between dissimilar metals creates galvanic corrosion and where ever possible should be avoided (**Jones, 1996a**). On the other hand, these constant modifications in engineering

design present many challenges of decreasing corrosion without creating exceedingly high costs. More anti-corrosion design tips are listed as follows.

1) *Materials selection* for corrosion-resistance is one critical part of the overall design process. Materials of construction should be economical yet provide adequate resistance to the specified service conditions.



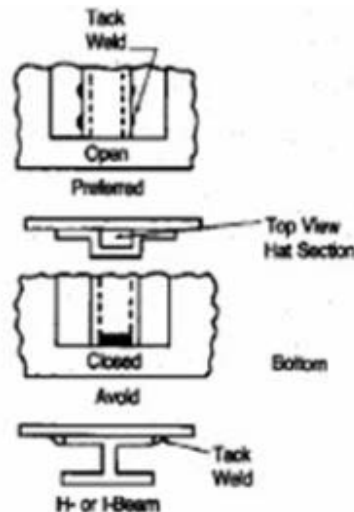
Metallic fasteners which join aluminum to a dissimilar metal should be made of an alloy cathodic to aluminum. Sacrificial protective coatings, typically formed by epoxy resins containing zinc, applied to steel fasteners are very effective



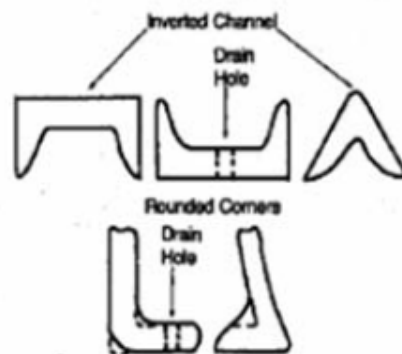
Coatings should be applied to both the anode and the cathode or to the cathode only. Damage to the coating on the anode would result in serious corrosion due to small anode-large cathode combination. Sealants should be applied to crevices for best results.

(Aluminum Association, Inc, 2001)

2) Structures designed for atmospheric corrosion resistance should always provide easy *drainage from all exposed surfaces*. General corrosion in the atmosphere is increased by any features that retain water. Channel and angle sections positioned to collect rainwater or debris may suffer increased corrosion, and proper design will thus position these parts to prevent water collection or include holes for drainage. The underside of constantly shaded panels may suffer increased corrosion, because time-of-wetness is increased when dew and other condensation are not readily evaporated by the sunlight. Insulation or lagging in contact with metal surfaces can also collect and retain condensation or rainwater.



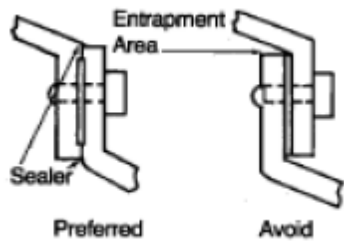
Hat section and H- or I-beam reinforcements are good designs but the hat section should be open at the bottom for easy drainage.



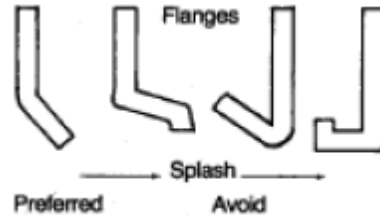
If not inverted, channels require drain holes to avoid entrapment areas; angle sections should have rounded corners, smooth tapers, and drain holes as indicated.

(Aluminum Association, Inc, 2001)

3) *Configuration of structures* should be as simple as possible. Design should allow maximum access for maintenance and repair painting. Box sections have poor access to coatings, collect water and debris, and maximize possibilities of corrosion. Edges and corners are difficult to coat uniformly, and thinly coated protrusions are susceptible to corrosion. On the other hand, the simple cylindrical structural members are preferred since they allow for ease and uniformity of paint application as well as convenient inspection.

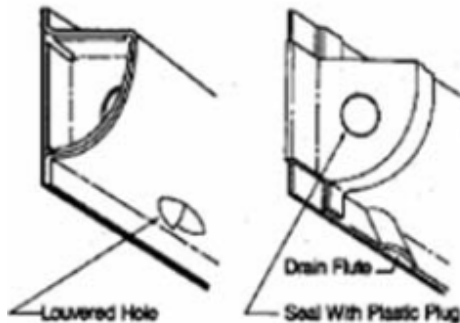


Design, and use of sealer, minimizes entrapment areas.

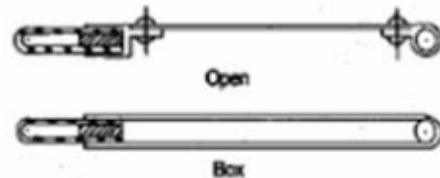


Flange orientation and design prevents entrapment of moisture and debris.

(Aluminum Association, Inc, 2001)



When box sections must be used, provide sufficient openings for the application and the drainage of protective coatings. Drain flutes and louvered holes should point down and to the rear of the vehicle. Crevices should be painted or sealed.



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(Aluminum Association, Inc, 2001)

4) *Stress corrosion cracking (SCC)* can be prevented by substituting a more resistant alloy, removing the tensile stress, or making the environment less aggressive. For example, in SCC of austenitic stainless steel by chlorides, substitution of ferritic or duplex stainless steels will often (but not always) eliminate the problem. The ferritic stainless steels may subject to pitting, but the duplex grades are

more resistant. Stress-relief annealing will reduce tensile stresses to below-threshold levels in many instances.

5) *Corrosion fatigue cracking (CFC)* can be prevented by eliminating cyclic stress or making the environment less aggressive. Vibrational stresses can be suppressed by a more rigid design. Removal of notches and other stress-concentrating features can be helpful, when feasible. Rounded fillets and angles will also reduce stress concentrations.

6) *Galvanic corrosion* can be avoided by using the same type of metallic material for the same structure. If dissimilar alloys have to be used in electrical contact with each other, galvanic corrosion can be controlled by selection of alloys that are adjacent to each other in the galvanic series. In other unavoidable couples, the anode alloy should be large in area compared to the cathode. Both members of a galvanic couple should be coated, never the anode alone, to avoid any small anode area at coating defects. If feasible, dissimilar alloys should be electrically insulated from each other at their junction. In atmospheric corrosion, continuous moisture drippage should not be allowed to carry corrosion products from a more noble to a more active metal to cause pitting of the latter (e.g. from copper to zinc-galvanized rain gutters or aluminum siding). Crevices between dissimilar alloys should be avoided, under which the corrosion is more serious than galvanic corrosion or crevice corrosion alone.

7) *Crevice corrosion* can be minimized by design of joints and junctions that minimize crevices. Welded joints are thus preferable to bolted and riveted joints, but the welds must be properly designed and constructed to eliminate crevices. Gaskets must be properly sized to minimize crevices exposed to the corrosive solution and should not use absorbent or permeable material. Sealing compounds and inhibitive coatings on flange faces may also be helpful. Both crevice and pitting corrosion may be expected to increase in stagnant or slow-flowing solutions, where deposits and corrosion products can accumulate to create crevices. Periodic cleaning may be necessary to remove deposits. Tanks should be designed for complete drainage.

8) *Erosion-corrosion* and *cavitation* are amenable to mitigation by design to reduce velocity and turbulence, as far as possible. Flow-channel dimensions and pumping capacity can be adjusted to minimize capacity. Abrupt changes in flow direction should be avoided, using maximum-radius elbows, and eliminating right-angle T-junctions, when possible. Baffle plates or deflectors may be helpful in diverting or shielding surfaces from erosive streams. Abrupt changes in channel dimensions should be avoided with tapered reducers. Careful welding technique is needed to prevent weld-bead penetration into the flow bath, creating turbulence and increased erosion-corrosion. A section of more resistant material may be required downstream from any devices creating turbulence, such as valves, pumps, or flow measuring orifice plates. Similarly, valves and pumps themselves should be constructed from resistant material.

3. Maintenance Practices

Maintenance practices include a wide variety of methods and procedures that may involve routine washing, reapplication of coatings, grit blasting, mechanical removal of rust, or the use of rust remover.

Sharman compared the efficiency of a newly developed biodegradable rust remover and mechanical rust remover. It has been found that this product creates an inexpensive method of removing rust and improving the quality of the surface of the steel. After the use of this product, coating adhesion was greatly improved causing an increase in performance of the coating thus increasing the service life of the material. This rust remover allows for a great alternative to grit blasting and mechanical removal of rust especially in situations where grit blasting may be prohibited or unusable for safety and environmental reasons (Sharman, 2009a).

Another family of methods that can be effective may be classed as surface protection. If some sort of barrier can be placed over any metal surfaces, then the corrosive chemicals can never make contact with the metal surface, and thus corrosion cannot occur. This can be achieved in a number of

different ways. First, surface treatments such as applying a coat of paint reduce the contact between the metal and moisture thereby preventing corrosion. Passivation of the surface may also be considered but the use of this approach is limited to those materials for which passivation are a possibility **(Kruger, 2000)**.

Adding inhibitors to ice control chemicals could be another methodology to minimize corrosion, there are a number of issues that remain to be resolved regarding this approach in order to ascertain the degree to which this measure is efficient and effective. Tests measuring the corrosivity of various chemicals, with and without inhibitors, provide very different results depending on the test used, the concentration of the chemical tested, and whether the test is conducted in the laboratory or the field. There are some practitioners who are firmly convinced that inhibitors reduce corrosion in maintenance equipment, and others who do not believe they are effective at all. No consensus exists as to how much the use of such inhibitors extends the service life of equipment thus making any calculation of benefit – cost ratios currently impossible. **(Nixon and Xiong, 2009)** Adding inhibitors to ice control chemicals have the potential to reduce the corrosion rate on vehicles, but for other equipment that not close to the ground, a better way to minimize corrosion is needed.

There does seem to be a consensus that vehicle washing is a very effective way to reduce equipment corrosion. At least in concept, the options for a washing program would seem to range from a rag and bucket through to a fully automated system. However, in practice an effective wash program would require at least some sort of low volume high pressure system. Fully automated systems are likely to cost in the range of \$1 to 5 million (depending on site details) but some of that cost is associated with disposal of the wash water. The disposal system must handle issues such as oil and grease in the water, and ensure that in appropriate contaminants do not get passed into the storm water system. Of course, any wash system, whether in a fully automated standalone facility or using a low volume high pressure system needs to include appropriate waste water disposal facilities, so that part of the cost is common to all wash systems. Nonetheless, it is clear that a fully automated system is very expensive. Assuming a twenty year life, annual savings generated by such a system over and above other simpler wash systems would have to be of the order of \$100,000 to 500,000. Clearly such systems make more sense at locations where many vehicles are stored, since this reduces the per-vehicle savings needed significantly, but such systems are unlikely to be viable at locations with less than 20 vehicles. However, such automated systems may offer savings over and above life extension savings. It may take considerably less time to move a truck through an automated wash facility than to wash it with a low volume high pressure system by hand, for example, and that reduced time translates into potentially significant labor savings. **(Nixon and Xiong, 2009)**

A better design and operational changes is always crucial for reduce corrosion rate, here are some examples of how equipment could be improved, especially for winter maintenance trucks:

- Use weather tight electrical connections;
- Position wiring to reduce damage to the outside casing of wires;
- Do not probe the wires to test for continuity;
- Use dielectric silicone for sealing damaged areas or connections.
- Open up closed areas (e.g. pillars) and allow them to flush out easily;
- Use welds to close and seal off certain areas that are difficult to drain;
- Caulk welds prior to painting;
- Do not apply paint to the rubber seals around lights;
- Consider buying stainless steel truck boxes, pre-wetting tanks, and sanders.

Finally, apply coatings to various equipment could also have some significant effect. There are clearly a number of coatings available that may be very effective at minimizing corrosion on winter maintenance equipment. There is an extensive literature on the performance of coatings. A search of TRIS using the terms “corrosion” and “coating” generated nearly 1,000 references. Areas within these references included coatings for bridges, for ships and marine structures, for pipelines,

and for railroad cars, and certainly some of the information in these references has some general relevance for winter maintenance equipment. (Nixon and Xiong, 2009)

Conclusions

In this chapter, some advantages of choosing materials for the purpose of corrosion prevention were presented. These design techniques are becoming a crucial aspect within many industries. The importance of improving design and implementing maintenance practices can combine to dramatically reduce the harmful effects of corrosion.

References

Adjorlolo, A. A., Marceau, J. A., “Commercial Aircraft.” Corrosion Tests and Standards: Application and Interpretation, Second Edition, 2005, 687-692.

Aluminum Association, Inc. “Aluminum: The Corrosion Resistant Automotive Material.” 2001.

Agarwala, V. S., “Control of Corrosion and Service Life.” Corrosion 2004.

Jones, D. A., Principles and Prevention of Corrosion. 2nd Ed. Prentice Hall, NJ, USA, 1996.

Kruger, J. (2000). “Passivity,” Ch. 9, pp. 165-172, in Uhlig’s Corrosion Handbook, 2nd Edition, Ed. R. W. Revie, John Wiley & Sons, New York, NY

Oliver, D. C., Sephton, M., “External Corrosion Resistance of Steel and Ferritic Stainless Steel Exhaust Systems.” The Journal of the South African Institute of Mining and Metallurgy, 2003, 93-100.

Reboul, M. C., Baroux, B., “Metallurgical Aspects of Corrosion Resistance of Aluminum Alloys.” Materials and Corrosion 2011, 62, (3).

Sharman, S., “Evaluation & Performance of Chemical Surface Treatments for Maintenance.” Corrosion 2009.

Uchida, M., Mochizuki, K., “Corrosion Behavior of Vehicles Operated in North America for 5 Years.” *Kawasaki Steel Giho*, 2000, 32 (1), 26-31.

Wilfrid A. Nixon and Jing Xiong. “Investigation of materials for the reduction and prevention of corrosion on highway maintenance equipment” IIHR Technical Report # 472, May 2009

Chapter 4. Coating Practices for Corrosion Prevention

Some metals and alloys, such as steel, aluminum and magnesium are widely used in maintenance and vehicles used by transportation agencies, which are often at the risk of corrosion associated economic loss [1]. Several methods have been established to prevent or protect metals from corrosion, such as barrier protection [2-16], galvanization [17-19], and cathodic protection [20-25]. The corrosion resistant coatings have attracted many attentions for many years due to its simplicity and efficiency [26-28]. The Numerous corrosion coatings have been developed and tested in an attempt to combat the harmful effects of corrosion on metal. Due to the variations in the physical and chemical properties of each of the different types of metals and alloys, the protection provided by each coating is dependent on the type of metal it is applied to and the environment in which it is exposed. This review will focus on environments consisting of common outside temperature, near neutral pH conditions, and in the presence of chlorides. With advancements in materials science, new corrosion coating systems are being developed. The development of these coatings is focused on enhanced functionality comprising corrosion protection and adhesion, environmentally friendly materials, corrosion and mechanical damage detection, improved fatigue resistance, and water resistant [29].

The widespread use of metals in corrosion prone environments has led to extensive research projects focused on developing coatings that protect against corrosion. These coatings must meet many requirements including: long-lasting, easy application, environmentally friendly, cost-effective, and high performance. Coatings based on metals, polymers, and various epoxies have been developed in addition to already produced commercial products. A review of the performance tests performed and their respective results are discussed.

1. Use of Coatings and Their Anti-corrosion Mechanisms

Corrosion protection coatings are generally based upon barrier protection, inhibitive coatings, or anodically active metal coatings. Barrier protection coatings cause oxygen deprivation or resistance inhibition. Inhibitive coatings alter the chemistry at the surface of the metal substrate. Anodically active metal coatings are usually made of zinc and due to their anodic activity level they are able to prevent electrical current from discharging from the substrate and causing galvanic corrosion. The zinc sacrificially corrodes, forming a corrosion product that provides protection similar to a barrier coating [30].

Certain coating systems have been commonly used to protect the metallic surfaces of vehicles from corrosion. Some common coating systems include conversion, electrocoating, metallic, organic, wax, autodeposition, and powder. Conversion coatings such as phosphate conversion coatings improve the ability of paint to adhere to the metal surface. Electrocoating is based on the use of electrically charged particles, which are dissolved within a tank. A conductive piece of metal is submerged in the tank in order to deposit the charged particles on its surface. Metallic coating is the application of a metal, often zinc or aluminum, via hot-dipping, electroplating, or mechanical plating. Recently, research in the area of organic coatings has provided alternative coating systems to potentially replace some of the traditional coatings that don't meet environmental standards. Organic coatings inhibit the transfer of charge from the metal to the corrosion inducing solution. Waxes are generally applied by melting the wax and subsequent dipping of the metal object into it. Autodeposition is based on a chemical reaction that causes deposition to take place. A powder coating is applied by spreading a dry powder on the metal to be coated. The dry powder is then heated causing the powder to create a film [31]. These coatings all prevent direct interaction between the metal and the corrosive environment, therefore impeding corrosion.

Sitaram et al. [32] have found that a general approach to coating systems often involves the application of three types of layers. Most commonly, the first layer consists of a metal oxide that inhibits corrosion. The next layer is a primer that contains inhibitors in order to provide cathodic protection to the metal. The top layer is generally a barrier that separates and protects the underlying coatings from the surroundings.

A study focused on the corrosion of automobiles found that the main factor influencing perforation corrosion was coating weight; this finding was independent of the type of coating [33]. A different study found that the thickness of the coating does not determine the amount of coating protection it will provide. It was found that an aluminum coating, a couple micrometers thick, protected steel better than cadmium and chromate-coatings that were tens of micrometers thick on steel samples [34]. It has been concluded that increasing the thickness of a certain coating will generally increase its corrosion protection, but the corrosion protection provided by two different types of coatings cannot be related solely based on thickness.

In addition, surface preparation is a key component in the success of corrosion protection coatings. The ability of the coating to adhere to the metal surface is directly related to the corrosion protection performance. The coating performance is significantly enhanced over a surface containing little or no contaminants [35].

When replacing a coating that is no longer environmentally acceptable, it is important that special attention is given to the corrosion behavior differences of the coatings to ensure that the new coating is an acceptable alternative. For example, many zinc-nickel alloys have been used to replace cadmium layers but issues arise due to the differences in their corrosion behavior. Zinc-nickel alloys exhibit localized corrosion and cracking, while cadmium layers are susceptible to uniform corrosion [36]. The differences in corrosion behavior will play a crucial role when providing the necessary corrosion protection system.

Many coatings methods have been used in the passivation of steel surfaces. Most of the effective corrosion protection systems for metals were metallic coatings, which contained chromates [37-39]. When chromate coatings are applied, hexavalent chromium compounds, loosely bonded in the film, are slowly leached on exposure to aqueous media, healing scratches and other defects. The chromate ions can interact with the metal surface forming a $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ solid hydrated conversion coatings. Organic coating is regarded as the most cost-effective measure for metals and alloys protection against corrosion. The protective properties of organic coatings on metal substrates may be attributed to a barrier and an electrochemical mechanism. As organic coatings typically have a high resistance to ionic conductivity, they offer good barrier properties and retard the diffusion of chemical species to and from the metal surface [40-42]. By adding chemically inert pigments this effect can be increased. The protective coating properties essentially are determined by the rate of water and oxygen diffusion through the insulating layer, promoted by the osmotic pressure in the pores and capillaries of the coating. In recent years, ceramics-based coatings for metals protection such as sol-gel coatings have emerged as versatile methods for substitution of the chromate pretreatments [43, 44]. Sol-gel technology can offer various ways to prepare functional coatings with different properties. Sol-gel protective coatings have shown excellent chemical stability, oxidation control and enhanced corrosion resistance for metal substrates. Further, the sol-gel method is an environmentally friendly technique of surface protection and had showed the potential for the replacement of toxic pretreatments and coatings which have traditionally been used for increasing corrosion resistance of metals.

Due to their advanced mechanical and physical properties, nanostructure materials have been the focus of many researchers attempting to create advanced corrosion resistant coatings [45-48]. Work

has focused on the types, production, and applications of various nanostructure coatings. Saji and Thomas [49] have demonstrated that a polymer nanocomposite coating can effectively combine the benefits of organic polymers, such as elasticity and water resistance to that of advanced inorganic materials, such as hardness and permeability. In addition to these advantages, nanomaterials also remove the need to use components that may have negative effects on the environment.

2. Coatings for Steel

2.1. Metallic Coatings

Metallic coatings have been widely used to protect against the corrosion of metals. Metallic coatings have two functions. The coating first acts as a barrier and also provides cathodic protection by galvanically corroding. Metallic coatings often consist of zinc or zinc containing alloys that have been applied by hot-dipping or electrodeposition. Surface cleaning is essential to ensure electrical contact between zinc particles and the coated surface. Results of studies focusing on these coatings and their corrosion protection relative to some of the other anticorrosion coatings are presented.

Stainless steel, hot-dip galvanized, zinc-rich primer with epoxy topcoat, and phenolic epoxy-coated steel were exposed to chlorides from the ocean air. Galvanized steel exhibited complete corrosion protection during the test period. The zinc-rich primer with epoxy topcoat and the phenolic epoxy-coated steel both provided good protection but suffered from corrosion at the scribes. Stainless steel exhibited localized corrosion and rust staining [50].

Galvanized zinc coatings have been very common within the automotive industry for many years. However, new zinc coatings with better performance are desired. Recent research shows promising results of magnesium-zinc coatings as an alternative. Corrosion protection of a Zn-Al-Mg alloy coating was compared to that of hot dip galvanized zinc coating. These were tested in an array of conditions including the following environments: chloride, chloride free, neutral pH, acidic pH, constant humidity, and cyclic humidity levels. The Zn-Al-Mg alloy provided better protection due to the formation of a zinc aluminum carbonate hydroxide layer [51]. Zinc-Aluminum-Magnesium coated steel was found to provide much more corrosion protection than zinc coated steel in chloride containing environments due to the formation of a long lasting aluminum rich oxide layer [51].

Another study found that zinc magnesium coated steel protected about three times better than electro-galvanized and hot dip galvanized steel. The improvement is attributed to the formation of magnesium hydroxide on the surface, which slows oxygen reduction reactions and enables the formation of a protective simonkolleite. Corrosion resistance of zinc-magnesium coated steel [52, 53]. Testing at the Kennedy Space Center (KSC) found that inorganic zinc rich primers performed better than organic zinc rich primers in the corrosive coastal environment [54].

To find the most effective coating system, corrosion resistance of certain coatings must be compared. Coating systems are comprised of a sacrificial metallic layer, then a sealer or conversion layer, followed by a primer and lastly a topcoat. Schmidt et al. tested 16 different coating systems by immersion testing in artificial seawater. Steel exposed to marine conditions exhibited good barrier protection when coated with ZnPhos + E-coat + solvent-based primer/topcoat. Thermal zinc spray coatings provided the best sacrificial protection, performing significantly better at the scribe than those without a sacrificial layer [55]. Steel sheets coated with either 55% Zn-Al alloy or traditional galvanized zinc, were exposed to atmospheric corrosion testing in Bandar Abbas. The testing found that galvanized steel corroded at a rate of 1.7-2.3 times greater than the Zn-Al coating. Both coatings experienced uniform general corrosion. However, the Zn-Al coating experienced denser corrosion within its interdendritic regions composed of Zn than within its dendritic Al regions. The aluminum-

zinc sulfate corrosion product associated with the Zn-Al coating adheres better than the galvanized zinc corrosion product, leading to better corrosion protection [56].

Material selection of aircraft components is focused on fatigue and corrosion properties since fatigue and corrosion are the primary failure modes of structural components. Coating systems are crucial on aircraft thus research plays an important role in determining the most effective corrosion protection systems. Steel samples with varying types and thicknesses of coatings were exposed to acetate and formate-based deicers commonly used on aircraft. It was determined that the aluminum coated steel performed the best. Cadmium-coated chromate-treated steel was found to undergo general corrosion. Difficulty producing a consistent and defect free chromate coating exposed the cadmium, which undergoes anodic dissolution that developed into general corrosion and consequent substrate exposure. An alternate aluminum coating for steel was also tested. Results showed the formation of a protective film on the surface, likely due to inhibitors included in the deicers, along with periodic localized corrosion [34].

Due to the environmental concerns associated with the use of cadmium and chromium coatings, new developments are crucial, and new zinc-nickel alloy coatings have been developed. These alloys are composed of 85-95% by weight zinc and 5-15% by weight nickel. In addition to replacing cadmium, zinc-nickel alloys having 6-15% by weight nickel have also been used to replace hexavalent-chromium (chromate phase) for toxicity reasons. The hexavalent-chromium replacing coatings consist of three layers: the first is a zinc-nickel alloy layer, on top of that is a trivalent chromate layer, and finally a resin layer. Lastly a binder containing phosphate is used to prevent the chromate phase production [57].

2.2. Organic coatings

Recently, significant research, focused on polymer coatings, has shown many potential applications for polymer coatings as corrosion protection systems. It has been observed that effective passivation of iron occurred with the use of conductive polymers. For selected polymers, the coating thickness, thermal treatment, methods of preparation and application have been analyzed and reported.

Herrasti and Ocon [58] investigated the corrosion protection of polypyrrole and polypyrrole/carboxymethylcellulose (Ppy/CMC) coatings on stainless steel. The interface between the metal and coating remained stable for long periods of time in the presence of 3% NaCl solution. The Ppy/CMC's compact framework was found to attribute to stability. When exposed to low current density, uniform films and significant corrosion protection were observed; however, when exposed to high current density, corrosion protection was minimal. Additionally, thermal treatment up to 150°C increased corrosion protection whereas; higher temperatures caused damage to the structure of the film. Consistent with other literature, successful corrosion protection using conductive polymers was observed.

Electropolymerization of poly(o-phenylenediamine) (PoPD) onto stainless steel using cyclic voltammetry from an acidic solution containing the monomer was performed to create 100 layers, each layer was about 1 micrometer thick. After testing the coating, the surface was almost free from pitting corrosion [59]. The corrosion protection is associated with the passive film that forms beneath the PoPD. This passive film contains iron (Fe), chromium (Cr), and nickel (Ni) hydroxides, which make up the majority of the stainless steel surface composition. The PoPD creates a barrier between the solution and the passive film on the surface of the stainless steel, resulting in significant pitting resistance in the presence of 3% NaCl [60].

Advancements in sol-gel technology have enabled potential corrosion protection applications with numerous advantages. Sol-gel-derived films offer good adhesion to metallic surfaces, low cost, low environmental impact, and simple application procedures. However, more research is needed to determine the best formulation for high performance corrosion resistance. Current approaches involve the incorporation of controlled release corrosion inhibitors. A sol-gel coating combined with an encapsulated corrosion inhibitor on mild steel was examined. The corrosion inhibitor cerium nitrate was encapsulated within a hydrophobic sol-gel coating enabling a long-term, controlled release. Cerium nitrate was selected due to its low price, environmental safety, and effectiveness. It was found that the encapsulation of cerium nitrate in the sol-gel improved corrosion protection through the controlled release and formation of cerium hydroxide, which interrupted the reaction at the cathodic sites. It was also found that using multiple layers increased the corrosion resistance and that when cured at 250°C an optimal coating thickness of 3-4 micrometers was obtained [61].

Hydrophobic treatment, a recent corrosion protection method, applied to steels provides an effective barrier against moisture on the metal surface and electrically insulates the underlying metal. Thus a hydrophobic fluoropolymer film, deposited on carbon steel using inductively coupled radio frequency plasma and the carrier gas octafluorocyclobutane, is proposed as a corrosion protection system. Fluoropolymer films offer low surface energy, good thermal stability, and chemical resistance. The resulting films adhered well to the steel surface and were hydrophobic. The optimal thickness of 90 nm resulted in a cost-effective and successful approach of corrosion protection. Figure 1 displays the physical effect of steel when using the fluoropolymer film exposed to 3% NaCl solution [62]

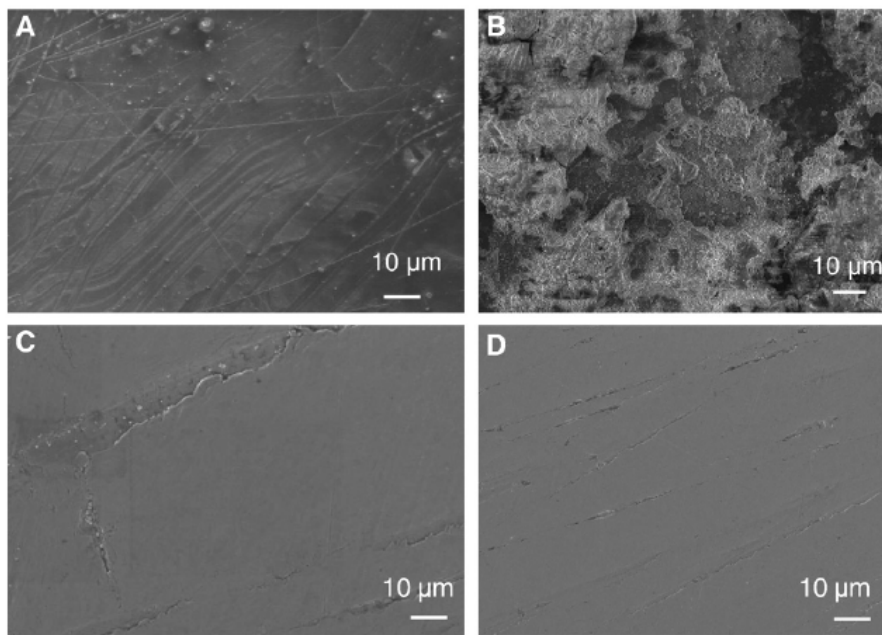


Figure 1: SEM images of (A) polished carbon steel substrate, (B) polished carbon steel substrate after immersion for 1 month in 3% NaCl, (C) carbon steel coated with 90 nm thick fluoropolymer coating and (D) carbon steel coated with 90 nm thick fluoropolymer coating and after immersion for 1 month in 3% NaCl [62].

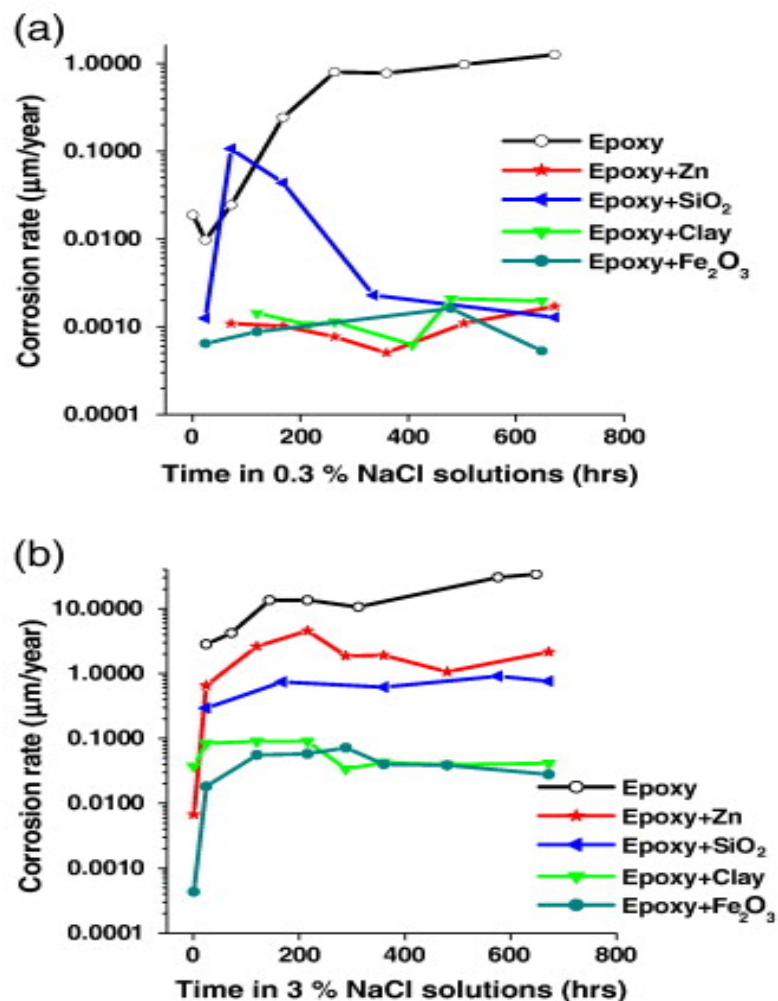


Figure 2. Temporal evolution of corrosion rate of epoxy-coated steel in (a) 0.3 wt.% NaCl solution, and (b) 3 wt.% NaCl solution, as a function of nanoparticles.

It is clear that many different polymers have been developed with successful results. Advances have found that combining the polymer coatings with inhibitors leads to additional corrosion protection; in some cases these coatings are self-healing. Further testing focused on the comparison of the polymer coatings with one another and on the length of time corrosion protection is provided, specifically in the form of on-vehicle or field-testing should be performed.

Epoxy coatings offer a wide variety of benefits and are often effective when used as corrosion protective systems, which can be attributed to their excellent chemical resistance, strong adhesion, and good electrical insulating properties. Epoxy coatings protect against corrosion by forming a physical barrier and when integrated with corrosion inhibitors, resist attack of aggressive species. It has been determined when nanoparticles are incorporated into epoxy resins, corrosion rate is significantly reduced. Shi et al. have proposed that the nanoparticles occupy small defects and can increase the cross-linking density causing improved durability of the coating. Shi et al. investigated the effects of corrosion of steel when integrating Zn, SiO₂, Fe₂O₃ and clay nanoparticles with epoxy coating. After a 28 day immersion test in 0.03% and 3% NaCl solution, epoxy with clay and Fe₂O₃

were determined to be the most effective corrosion protection coatings which is consistent with Figure 2 [16].

Additional corrosion prevention coating systems combined organic compounds and metals with epoxies and acrylics have been developed. These types of coatings are generally applied while wet and adhere to the surface after drying. The less demanding application makes them more suitable to be produced and sold commercially rather than requiring manufacturer application. Epoxies offer great versatility and good performance.

In the past several years, great advancement has been developed for epoxy corrosion coating systems. Along with accelerated tests and atmospheric exposure, electrochemical data for the corrosion resistance of eight acrylic and epoxy coatings was collected. The following coating systems: epoxy-polyamide, homogeneous acrylic paint, epoxy-amine homogenous, and epoxy-acrylic heterogeneous in the presence of a zinc pigmented primer were tested for their corrosion protection of steel. It was found that the epoxy-polyamide systems provided the best protection. Intermediate protection was provided by the epoxy-amine homogeneous and epoxy-acrylic heterogeneous coatings. The homogeneous acrylic paint provided the worst corrosion protection, exhibiting blister formation and filiform corrosion. Correlations between atmospheric exposure and accelerated salt spray test were found [63].

Paint is a mixture of pigments and resins in a solvent, which after applied to a surface evaporates and causes a hardening effect. Resins are mostly made of polymers while pigments can be ceramic, metallic or composed of polymers. A study focused on the effects of manipulating concentrations of dispersant, anticorrosion pigment, and wollastonite in styrene-acrylic resin paints on the corrosion protection of carbon steel has been done. The paints were composed of 31% pigment by volume. Constant amounts of ethylene glycol, titanium oxide, water, rheological agent, inhibitor, and defoamer were used. The paint tested with 25% pigment volume concentration, 0.4% wollastonite, 0.40% zinc, and 0.41% dispersant by weight was found to provide the best corrosion protection. A paint consisting of 31% pigment volume concentration, 2.5% zinc, 2.5% wollastonite, and 0.42% dispersant provided decent protection. Table 1 displays the weight loss measurements of test panels using various coatings. The study found that zinc phosphate assisted in corrosion protection and that wollastonite improved the lifetime of the paint. It was also found that using the same amounts of zinc phosphate and wollastonite provided the best corrosion protection [64].

Table 1. Weight loss of test panels due to exposure to marine environment (Port of Barcelona) [64]

Time (month)	Weight loss of test panels coated with various paint formulations (g)								
	Alkyd	Chlorinated rubber	Polyurethane	Cataphoresis + polyurethane	Hot dip galvanizing	Temporary protection	Uncoated	Styrene acrylic	Acrylic
0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0.09	0.31	0	0
4	0	0	0	0	0	0.17	0.61	0	0
6	0	0	0	0	0	0.59	0.81	0	0.18
12	0.20	0	0	0	0	0.57	0.64	0	0.21
24	1.33	0.07	0.71	0	0.57	2.24	2.63	0.10	1.10
34	0.81	0.05	0.45	0.46	0.67	–	2.04	0.60	1.50

Research was focused on creating alternative anticorrosive paint pigments that can be used to replace toxic zinc chromate. Phosphates have been the most successful nontoxic corrosion inhibitive

pigments. Recent research has found advantages including low cost, nontoxic, and easy application of zinc phosphates as pigments in corrosion prevention systems. Three different types of alkyd paints were exposed to 3% NaCl solution. The paints were composed of the pigments calcium acid phosphate, micronized zinc phosphate, and zinc chromate. It was found that zinc phosphate provided the best protection followed by calcium acid phosphate, and zinc chromate respectively. The results show that divalent cation phosphate pigments are potential effective replacements for chromate coatings [65]. Similarly, the corrosion protection provided by zinc ethyl silicate was determined to display excellent barrier performance [66].

In less corrosive environments, single coat zinc-rich primers offer effective corrosion protection. However, an additional barrier layer is needed in more aggressive environments. Micaceous iron oxide and titanium dioxide are the most effective barrier pigments available. Micaceous iron oxide, titanium dioxide and chlorinated rubber, known for its high impermeability to water and corrosion causing ions, have been combined to create the topcoat. Application of a barrier finish coating on top of zinc-rich primer has been found to hinder corrosion of mild steel in the presence of 3% NaCl solution. The micaceous iron oxide and titanium dioxide pigments are used due to their excellent performance in barriers. The chlorinated rubber finish coats were produced by adding the two pigments independently and were implemented on a butyl titanate zinc rich primer, cashew nut shell liquid zinc rich primer, and an epoxy polyamide zinc rich primer. It was found that the organic zinc rich primer behaved differently than the inorganic primer, which was caused by the cathodic protection of the inorganic primer. Use of both micaceous iron oxide and titanium dioxide with zinc rich primer systems was found to be very effective, yet smaller pigment volume concentrations of micaceous iron oxide was found to be equally effective as larger pigment volume concentrations of titanium dioxide [67].

Specific issues involving the use of organic coatings are: non-uniform film distribution on the surface of the metal substrate, uneven crosslink density throughout the film, varying pigment concentration in the coating, and expansion/damage when exposed to gases/liquids. In order to combat these issues the use of multiple layers has been employed. Using multiple layers prevents areas with defects from overlapping, therefore ensuring that the entirety of the surface is coated. Another approach for mitigating the concerns with organic coating is the use of a primer and middle layer with wet adhesion and dense crosslinking along with a topcoat that is UV resistant and hydrophobic. Enhanced corrosion protection and chipping resistance was found to result from a coating system made up of an initial cation electrodeposition coating, followed by a liquid coating, next a powder coating, another liquid coating, and lastly a topcoat. One additional method to prevent pinholes and damage of organic coatings is the use of a resin that cures when exposed to UV light [68].

The effectiveness of organic coatings greatly depends on permeability, thickness, electrical properties, and adhesion to the substrate. These coatings prevent corrosion by acting as a physical barrier, inhibiting the corrosion process, or by increasing the electrical resistance. Four paint systems were used on galvanized steel to test their protection in 3.5% NaCl and in weathering tests. Two of the systems were composed of a primer (wash primer and high built primer) and special acrylic resins (containing micaceous iron oxide, zinc chrome pigments, and titanium dioxide pigments depending on the layer), while the other two systems were made up of an epoxy primer (wash primer and two-component primer) and a finishing coat of epoxy paint including zinc chromate and iron oxides. Systems 2 and 4 were composed of two layers, not having the additional wash primer layer that Systems 1 and 3 had. All of the systems performed better than galvanized steel alone. The three layer system composed of the wash primer, two-component epoxy primer (with zinc chromate and iron oxide), and two-component epoxy paint supplied the best corrosion protection. The two layer epoxy primer and epoxy paint system without the wash primer layer performed well but suffered from a lack

of coating adhesion. The acrylic resin system with the wash primer performed close to as well as the two layer epoxy coating mentioned previously and the acrylic resin system without the wash primer performed the worst. Table 2 displays the corrosion rates of steel using the various coatings [69].

Table 2. Corrosion rate of tested samples [69].

Corrosion current density (nA/cm ²)					
Exposure time (days)	Galvanized steel	System 1	System 2	System 3	System 4
1	0.1 x 10 ⁶	13.8	140.6	7.8	12.2
60	1 x 10 ⁶	26.3	562.3	12.6	23.9
120	30 x 10 ⁶	63.1	1585	13.3	54.9

The corrosion protection provided to steel by anticorrosion pigments containing aluminum polyphosphate was examined. It has been found that aluminum triphosphate can reduce the amount of corrosion and is strongly impacted by the pigment used. A downfall to the use of aluminum triphosphate is the need to bring its pH to a neutral value from its original acidic pH, finding a component to fill this task is difficult as many with high pH values cause issues with adhesion. The incorporation of aluminum triphosphate pigment at 10% vol was found to be optimal. Lastly, using pigments with barrier properties may be beneficial by adding additional barrier protection to the paint [70].

A study was performed that tested over 18 commercially available products for their ability to protect steel and iron. The focused requirements for high performance were the ability to protect for three years, removable, and environmentally friendly. It was found that Cosmoloid H80, Dinitrol Car/4941, LPS3, Rustilo 3000, SP400, and VpCI-386 performed the best. **Table 3** summarizes the results the corrosion testing and **Figure 3** contains images of the test panels before and after atmospheric exposure testing [71].

Table 3. Performance of surface treatments [71].

Surface treatment	Hardness of coating, marked with thumbnail?	Adhesion to Q panel (per cent of coating remaining on panel)	Percentage surface covered by corrosion after 504 h salt spray test, %	Visible changes in Danish weather for six months	Rate of corrosion by oxygen consumption after 70 days, $\mu\text{m}/\text{year}$
None (bare panel)			100	Corroded	130
Corroheat 4010	Yes	97	0	Discoloured	2.7
Cosmoloid H80	No	85	0	No change	<0.1
Dinitrol Car/4941	Yes	100	0	No change	0.7
Frigilene	No	100	50	Corroded	0.1
Incralac	No	90	8	Corroded	<0.1
LPS3	Yes	40	0	No change	0.1
Paraloid B72	No	86	8	Corroded	0.2
Paraloid B72 with 1% perfluorodecyl iodide	No	95	50	Corroded	0.4
Poligen ES91009	No	100	50	Discoloured/corroded	16.6
Renaissance wax	Yes	98	50	Corroded	1.9
Rustilo 2000	Yes	100	8	Corroded	...
Rustilo 3000	Yes	100	1	No change	0.4
Ship-2-Shore Industrial	Yes	Liquid, unable to measure adhesion	50	Corroded	1.9
SP400	Yes	95	0	No change	0.2
Tectyl 506 rust preventative	Yes	100	0.5	Discoloured	1.5
Tectyl Glasholder/Klar spray	Yes	100	50	Corroded	1.5
Tromm III	No	99	50	Corroded	3.5
VpCI-386 acrylic primer/topcoat	No	100	1	No change	0.1

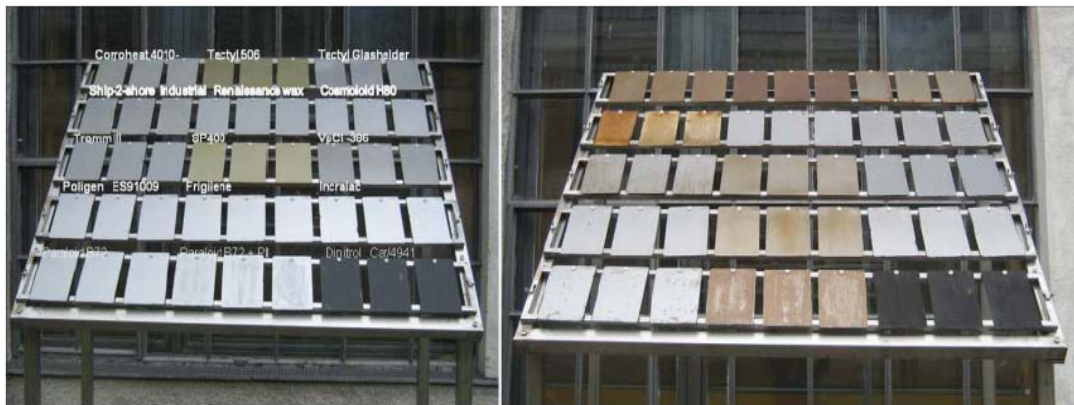


Figure 3: Three panels of each coating were subjected to atmospheric corrosion testing. The panels were mounted on two frames in June 2009 (left). The same panels show discoloration and the formation of corrosion by December 2009 (right) [71].

3. Coatings for Aluminum

Thus far the focus has been various coating systems used on steel, which have included metallic, polymer, and ceramic coatings. However, aluminum, which contains a high strength to weight ratio, is commonly used within the airline industry and becoming more popular in many other industries. Since corrosion affects various metals through different mechanisms, the design of corrosion coating systems is changed. Using a coating system on aluminum, which is susceptible to pitting corrosion, will prevent loss of structural integrity due to corrosion. Here the focus shifts from steel corrosion protection to aluminum protection.

An investigation of organic-inorganic composite materials for use in corrosion protection permits a better understanding of both organic and inorganic properties and how these properties can be utilized. These composite materials are able to combine diffusion barrier and the required flexibility gained from the inorganic network. These composite systems can contain SiOH or SiOR components, which creates stable complexes with the aluminum metal surface. **Figure 4** displays a schematic of a nanocomposite coating on aluminum. Evidence suggests that the formation of Si-O-Al is thermodynamically favored. A thin coat of 5-10 μm thick is applied and displays good corrosion protection after 240 hours of salt spray test. **Figure 5** shows the interface design concept for corrosion protective coatings on aluminum [72].

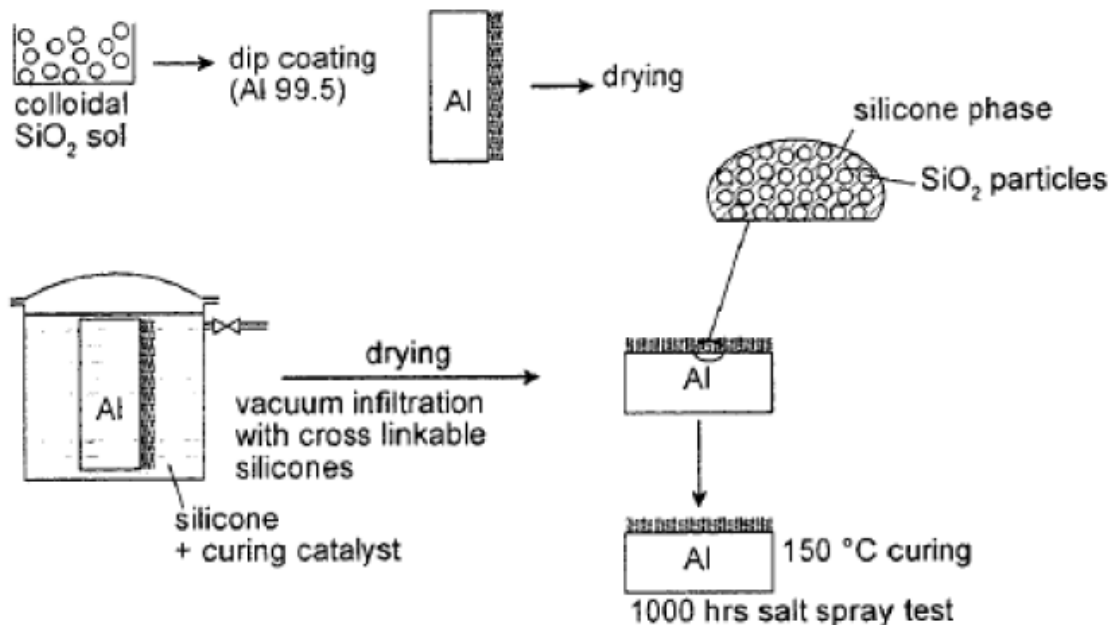


Figure 4. Schematics of a nanocomposite coating on aluminum.

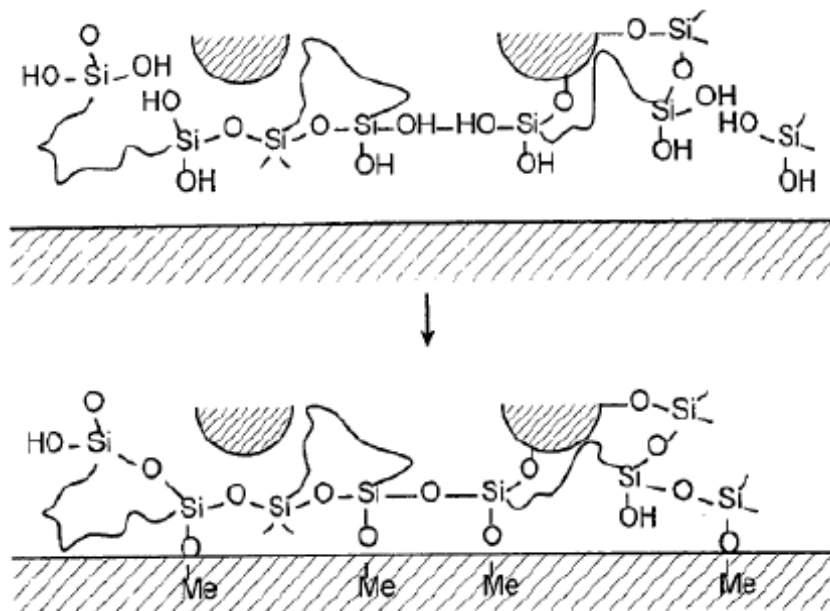


Figure 5. Concept of the interface design for corrosion-protective coatings on aluminum.

Another variety of organic-inorganic composite material used as a corrosion protection system consists of organically modified silicates. These are formed by the hydrolysis and condensation of modified silanes with alkoxide precursors. Metroke et al. studied the corrosion protection characteristics of 3-Glycidoxypropyltrimethoxysilane (GLYMO) modified Ormosils used as a coating on aluminum (shown in Figure 6). Electrochemical analysis was used to determine the corrosion potentials of abraded and deoxidized aluminum alloys exposed to 1 M sodium chloride solution. E_{cor} , corrosion potential, for abraded aluminum was -0.669 mV and -0.719 mV for deoxidized aluminum. It was determined that corrosion protection was related to organic content concentration and hydrolysis water content (W). Highest corrosion protection performance was observed with films with high organic content and low water content [73].

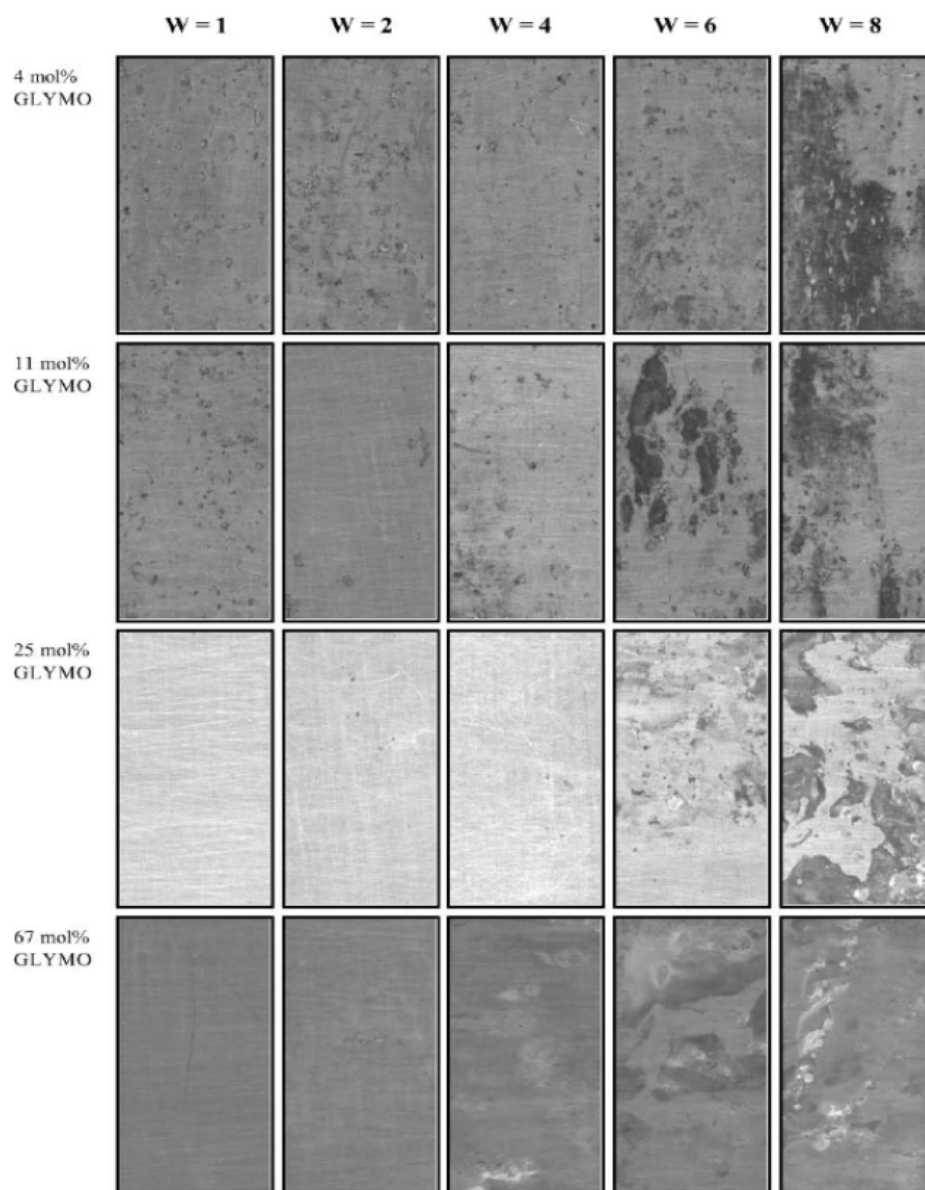


Figure 6. Results of 168 h salt spray tests for dip-coated 4, 11, 25, and 67% GLYMO Ormosils film as a function of hydrolysis water content. Images represent a 1 in. x 2 in. test coupon.

Surface treatment and coating deposition play crucial roles in the overall effectiveness of a coating system. Adhesion properties have been known to be directly related to coating performance. A synergistic approach is believed to be appropriate in order to obtain similar surface protection as conventional chromate coatings. Research on pseudoboehmite(PB)-silane hybrid coatings has shown the formation of a M-O-Si bond forms between the silanes and the metal surface. The PB coating increases the surface area and the porosity, leading to greater stability due to increased Al-O-Si bond density. The corrosion protection due to the coating was synergistic and was increased when the AA2024 was prepared by exposing it to boiling water. The corrosion protection from the PB coating was found to be better than a chromate coating on aluminum or alkali pretreatment [74]. Similarly, the study of AA2024-T3 coated with bis-sulfur silane found the interfacial layer contributed largely to the corrosion protection of the aluminum alloy due to the extremely cross-linked arrangement of the layer, high level of adhesion to the aluminum alloy, and lack of porosity in the layer. These characteristics block pitting by decreasing the transfer through the layer. Furthermore, the Al-O-Si bonds that form at the interface of the film stop the development of cathodic sites [75].

Nanoporous silica is one of many materials being explored for use in encapsulating and controlled release of corrosion inhibitors. Nanoporous silica is a ceramic whose pore size can be controlled and has other desirable traits such as small pore size distribution, stability both mechanically and thermally, environmentally friendly, and cost-effective. In particular, nanostructure silica particles with a core of cerium corrosion inhibitor have been successfully used to prevent the corrosion of AA2024-T3 in the presence of 0.05 M NaCl [76].

During the last few years, sol-gel films have been extensively studied for potential applications in corrosion prevention. Both active and passive corrosion protection offer important components to a corrosion protection system. Passive protection occurs with a barrier film preventing contact with corrosive species and active protection begins when a coating is damaged. The addition of corrosion inhibitors to hybrid sol-gels enables self-healing in addition to the barrier protection provided by the sol-gel. Cerium salts and 8-hydroxyquinoline were tested and found to provide active protection in while the sol-gel barrier provided passive protection. The addition of metal oxides to the siloxane strengthens the close-packed -Si-O-Si- bonds [77]. Another self-healing coating is based on pre-formed hybrid organo-silicate nano-particles with epoxy functional groups that are applied to the metal surface where they cross-link, a type of self-assembled nanophase particle (SNAP) coating process. These SNAP coatings exhibit good barrier protection and adhesion to aluminum alloys but perform poorly if damaged [78]. These hybrid organo-silicate coatings contain an inhibitor that is released at damaged locations of the coating, therefore providing self-healing protection. Several inhibitors, including mercaptobenzothiazole (MBT), mercaptobenzimidazole (MBI), mercaptobenzimidazole-sulfonate (MBISA), and thiosalicylic acid (TSA), have been tested. Two different methods for inhibitor storage and delivery, cyclodextrin-assisted molecular encapsulation and ion-exchange anchoring of the inhibitor, were also examined. Results showed that MBT and MBI, the non-ionizable inhibitors, encapsulated in their molecular forms or as inclusion complexes with β -cyclodextrin provided better protection than ionizable inhibitors, such as TSA and MBISA. At the equilibrium of the complex, the β -cyclodextrin encapsulation has a slow release and continues inhibitor transfer to corrosion locations [79]. These additions of inhibitors and encapsulation of inhibitors displays encouraging results in terms of adding inhibitors to barrier corrosion protection systems.

Sol-gel coatings provide good barrier protection but do not participate in active corrosion protection. The integration of nanoparticles into sol-gel films has been known to increase corrosion protection. A self-repairing coating for aluminum alloys based on cage like oil core/silica gel shell particles was created. The repairing agent, methylmethacrylate, and catalysts, potassium persulfate

and sodium thiosulfate, were encapsulated in the cage like microspheres as the microspheres were constructed. The microspheres were self-assembled on AA2024 and then coated in a sol-gel film. Analysis showed that the film worked as a primer with self-repairing capability [15].

The sol-gel method also can potentially offer a promising approach in the development of a corrosion protection system. The sol-gel preparation methods influence the properties of the coating and subsequently the corrosion protection. The increase in TPOZ hydrolysis time and temperature increased the amount of ZrO_2 nanoparticles within the sol-gel film. The ZrO_2 nanoparticles enhance corrosion protection and were also found to cause pore blocking of the film [80]. Similarly, Voevodin et al. evaluated the performance of a Zr-epoxy sol-gel coating which reinforced the many possible advantages of sol-gel coatings. The effectiveness of the sol-gel coatings is attributed to their ability for form inorganic-organic and hybrid networks [81].

Nano-engineering, engineering at the nano scale, may offer some valuable applications in corrosion prevention. It is proposed that nano-engineered coatings can use energy produced during the corrosion process to produce and distribute an inhibitor. A recently developed smart coating system utilizes corrosion energy to cause the release of corrosion inhibitor only when needed. Aluminum alloy 2024-T3 was protected using conducting polyaniline films and anionic inhibitors including Ce^{3+} and Cr(VI) and a couple types of polyaniline films. The Cr(VI) provided much better corrosion inhibition than the Ce^{3+} , it was also observed that the less porous polyaniline films provided better protection. Corrosion at the scribe causes the aluminum substrate to polarize the polyaniline film, resulting in inhibitor discharge and scribe protection [82].

The application method was also found to have a significant impact on the ability to coat surfaces; electrochemical deposition enables the coating of structures with intricate geometries much more effectively than dip and spin coating methods. The greater the hydrophobicity of the monomer the better the corrosion protection, displayed by phenyl trimethoxysilane performing much better than tetraethoxysilane [83].

Synergistic effects have been known to play an important role in the protection of metals against corrosion. More detail of this synergistic mechanism was revealed during the work of Kachurina et al. Corrosion of aluminum exposed to 0.35 wt % $(\text{NH}_4)_2\text{SO}_4$ and 0.05 wt % NaCl protected by a synergistic layer by layer organically-modified silicate coating was investigated. Individually both layer by layer (LBL) and organically-modified silicate (Ormosil) coatings cause passivation of the aluminum but neither individually provided much protection. By including cobalt (III) into the LBL as an active inhibitor and matching the LBL with the Ormosil topcoat, corrosion protection obtained was much better than that of either alone. This increased corrosion protection is due to the densely cross linked layer of clay composite that is produced at the juncture of the LBL and Ormosil layers. The Ormosil layer also keeps corrosion inhibitors from escaping the LBL [84].

The search for protective coating alternatives has led to the possibility of using zeolites, microporous crystalline aluminosilicates. It has been shown that coatings on aluminum alloy containing high-silica-zeolite contain exceptional corrosion resistance. It has been determined that the best corrosion resistance is obtained with a dense polycrystalline zeolite coating with no intercrystal porosity and no intracrystal porosity, which is usually achieved with the use of bulky organic molecules during synthesis. The corrosion protection provided by zeolite coatings to aluminum alloy 2024-T3 exposed to NaCl in salt fog testing was observed. It has been found that the bare zeolite coating provides good corrosion protection where the coating is been damaged, corrosion will concentrated in that area. Additionally, AA 2024-T3 samples coated with a complete zeolite coating of MFI (mordenite framework inverted) structure, a primer (Mil-PRF-23377 Type I Class C), and

both in the presence and absence of a topcoat (Mil-PRF-85285) were found to perform great, passing 3100 hours of salt-fog exposure without any issues with adhesion or corrosion at the scribe [85].

Experimentation on the effect of the type of thermal spray coating process to the corrosion protection of AA2024-T3 was conducted. Using powder flame spray, atmospheric plasma spray, and high velocity oxy fuel (HVOF) thermal spray coating processes a 99-99.8% Al coatings were applied to the aluminum substrate. Analysis of the mechanical properties, pre-corroded properties, microstructures, etc. show HVOF to be the most advantageous thermal spray process to use [76]. The HVOF can also be used to deposit a coating that contains corrosion inhibitors, further improving the corrosion resistance provided.

4. Coatings for Magnesium Alloys

Magnesium alloys are becoming more popular in various applications. Magnesium alloys are extremely lightweight, which makes it very useful within the aircraft and automotive industries. For maximum corrosion resistance, magnesium alloys must not contain any heavy-metal impurities. In addition, protective coating systems are recommended to improve corrosion resistance. A discussion of various techniques found to protect magnesium alloys against corrosion is presented.

Electrochemical plating is an economical and simple way to apply a metal coating to magnesium, which is much more complex than most metals due to its high reactivity. Magnesium quickly forms an oxide layer on its surface in the presence of oxygen, making a pretreatment that prevents this formation necessary. Zinc and nickel pretreatments have been used successfully. Electrochemical plating of magnesium alloys has proven difficult because of the intermetallics at grain boundaries result in inconsistent surface potential of the metal surface. The two methods of electrochemical plating, electroplating and electroless plating each have their disadvantages. Electroplating can suffer from uneven current density resulting in inconsistent plating thicknesses. Electroless plating faces issues with its short bath life and environmental concerns over disposal of the baths. The application of a Cu-Ni-Cr plating provides corrosion protection in mildly corrosive environments. However, a coating that can withstand corrosive high salt and marine conditions that would be necessary for adequate protection in the automotive industry has not yet been established [68].

Conversion coatings can also be used to protect magnesium from corrosion and provide an adhesive surface for an additional paint layer. Conversion coatings are applied using a chemical or electrochemical treatment process that chemically bonds a layer of oxides, phosphates, or chromates to the surface of magnesium. Conversion coatings add protection by providing a barrier that prevents transfer of electrons between the metal and the surrounding environment. In addition, corrosion inhibitors are also added to conversion coatings to increase corrosion resistance. Conversion coatings are extremely dependent on the cleaning and pretreatment of the surface they are applied to. The more detailed the cleaning processes the better the corrosion resistance. Chromate, fluorozirconate, and phosphate/permanganate have successfully been used to create quality conversion coatings. The downfall of many corrosion coatings is the use of toxic materials in the treatment solutions and finding coatings that will evenly coat the wide array of elements found in alloys [68]. Magnesium alloy AZ91D treated with a cerium conversion coating had improved resistance to localized corrosion. Cleaning and surface treatment of the metal substrate with potassium hydroxide inhibits active sites on the surface and prevents chloride ions from contacting the surface and forming an oxide layer. The presence of cerium shifts the pitting potential although the amount of inhibition in NaCl is very dependent on the cerium concentration [86].

Hydride coatings are yet another system of corrosion protection. Hydride coatings are applied by immersing the magnesium alloy in an alkaline solution. The magnesium acts as a cathode and after polishing, degreasing, and acid etching, the magnesium undergoes cathodic treatment creating the hydride coating. The hydride coating has been found to reduce the corrosion rate of AZ91D magnesium alloy by 33%, providing corrosion protection similar to that of a dichromate coating [68].

Anodizing can be used to create a stable oxide film on a metal surface using an electrolytic method. Benefits of anodizing include better paint adhesion and results in passivation of the surface. The resulting anodized coating consists of two layers and an outer sealing layer. The layer at the interface of the metal and the coating is thin and acts as a barrier; on top of this layer is an additional layer with a cellular structure. These cellular structures contain pores, the size and density of these pores determines the magnitude of protection provided. The oxide layer must then be sealed either by treatment such as boiling or steam, or using a lacquer. Hard anodizing is performed by reducing the temperature of the electrolyte and by intensifying the current density. Hard anodizing may also be performed when additional hardness and wear resistance is required. The addition of solid film lubricants increases the benefits of hard anodizing. As with all coatings, anodizing has its disadvantages such as flaws, inclusions, pores, and difficulty obtaining uniform current density, which can lead to uneven coatings. Furthermore, the coatings produced are ceramic material that often becomes brittle [68].

Laser surface alloying can be used to melt a metallic coating and metallic substrate using a powerful laser. Use of the laser surface alloying is favorable because it is very accurate, not limited by the geometry of the surface, and relatively inexpensive, and only affects the surface a few millimeters deep. The laser causes the coating and metal beneath to melt, blend, and re-solidify very fast. Research has found that the use of aluminum, copper, and chromate coatings when laser surface alloying results in increased corrosion prevention [68].

Organic/polymer coatings are generally applied as a topcoat of a coating system. The main purpose is to create a barrier between the protected metal and the surroundings, preventing the transfer of water, oxygen, charge, and ions. Many coatings are used in locations where damage is likely to occur. In order to create a long-lasting coating, self-repairing coatings have been developed. Self-repairing coatings often incorporate additives to the coating, such as inhibitors, or sacrificial compounds. For example, the corrosion protection of magnesium is enhanced using a coating based on a phenolic resin primer and zinc chromate. Another study found that adding an inhibiting leachable pigment and an ion reactive pigment could reduce corrosion. In this case chromate acted as the inhibiting leachable pigment and small spherical aluminum particles acted as the ion reactive pigment. The protection is attributed to the fact that the spherical particles interact with ions that cause corrosion, controlling the pH and the chromate is released at damaged areas filling gaps in the coating [68].

The corrosion protection of AZ31B magnesium alloy exposed to 0.005M NaCl was heightened via the application of a sol-gel coating. More specifically, the sol-gel coating was created through copolymerization of epoxy-siloxane and zirconium alkoxides. The addition of tris(trimethylsilyl) phosphate provides supplemental corrosion protection through a chemical interaction with the magnesium, which leads to a more stable film. The corrosion protection of the coating system is also attributed to the Mg-O-P bonds that are formed; these bonds are hydrolytically stable and show excellent adhesion of the coating to the magnesium alloy [87].

Magnesium and its alloys offer high strength to weight ratios and high thermal conductivity, which make it a valuable option in various applications. Conversely, magnesium alloys are highly vulnerable to galvanic corrosion, which has greatly restricted its extensive use. Plating, anodizing,

conversion coating and polymer coating are a few techniques commonly used to protect against corrosion. However, recent research has investigated the use of poly(ether imides) as a corrosion protection polymer coating system. This research has yielded some promising results and demonstrated the effectiveness of poly(ether imides) to reduce corrosion rates [88].

5. Coatings for Other Metals

5.1. Metallic Coatings

Hexavalent-chromium coatings have been found to be extremely effective at providing corrosion protection. However, recent environmental concerns about the use of hexavalent-chromium have led to the banning of its use and the development of alternative coatings. However, research to improve other phases of chromium for use in coatings is being conducted. One approach is to focus on improving the electroplating bath, which includes a water soluble trivalent chromium salt, a complexant, hydrogen ion source to maintain a pH 2.8-4.2, pH buffering compound, and a sulfur-containing organic compound [89]. A military study approves the use of trivalent chromium pretreatment (TCP) as a hexavalent-chromium replacement as long as a chromated primer is used. It is important to note that compared to other hexavalent-chromium alternatives, TCP requires very tight control during the application process and specific surface preparation [90]. Focusing on the bath and pretreatment of the metal greatly improves coating effectiveness. Another alternative to hexavalent-chromium is a conversion coating that uses ferrate as the oxidizing agent. The coating consists of 0.0166-1.66% by weight ferrate ion and another transition metal oxyanion. The use of vanadate as the transition metal oxyanion/corrosion resistant material shows promising results and has been the issue of recent conversion coating related patents [57].

Another alternative to hexavalent chromium coatings is the aluminum pigmented ceramic coating. The coating is composed of atomized aluminum pigments and an acidic phosphate and dichromate binder. In addition to taking on the normal role of a binder, the dichromate passivates the aluminum particles and ferrous substrate, reducing the likelihood of a reaction with phosphate. The coating can be turned galvanically active and used as a sacrificial coating by bombarding with an abrasive. Finally, this coating can be sealed with an inorganic topcoat. This coating has nearly equal attributes to those of chromium containing aluminum ceramic coatings, making it an excellent replacement [91].

Similar to hexavalent-chromium, the environmental concerns associated with cadmium coatings have led to the development of alternatives. The Joint Cadmium Alternatives Team has been working on developing alternatives for the military. Their discoveries have shown that AlumiPlate, an electroplated aluminum, provides the greatest protection. The use of low hydrogen embrittlement ZnNi alloy plating (LHE ZnNi) currently performs equally to Cd nevertheless a new process for depositing nanostructured ZnNi via pulse electroplating is being examined [90]. Another area of research is focused on cold spray coatings. These cold spray coatings are Al and Al alloys that are applied to corroded and damaged areas to supply a sacrificial coating [90].

In attempt to reduce pitting corrosion of aluminum in NaCl, micro-crystallization and magnetron sputtering has been used to deposit aluminum film. Pure aluminum microcrystals about 400 nm in diameter were used to form the microcrystalline aluminum film. The film undergoes passivation and displays better corrosion resistance than cast aluminum. It is common for the pit initiation rate to increase and metastable pits to form. The resulting metastable pits are likely to form stable pits, preventing further pit growth. Therefore, the use of a microcrystalline aluminum film improves the repassivation and pitting resistance of aluminum [92].

Thermal spray coatings consisting of Zn, Al, or Zn-Al alloys are often used for corrosion protection. Most often these metals are applied via arc or flame spraying. It has been found that the preparation of the substrate surface and the application process play a large role in the uniformity and adhesion of the coating. Each of the following factors, which includes alloy composition, preparation of the surface, application, sealer, the conditions the object is to be employed, and any environmental issues that may arise must be examined in order to create the ideal coating system. Due to the porous nature of thermal sprayed coatings, it is very necessary to apply a sealant or paint. Optimally, a wash primer such as zinc-chromate is applied on the thermal spray coating, a sealer such as phenolic resins, polyester resins, or polyvinyl chloride is applied over the wash primer and a polyurethane or epoxy topcoat is often applied last. In all, a properly applied thermal spray coating can provide corrosion protection for approximately 10-20 years when supplemented with infrequent servicing [93].

5.2. Polymers Coatings

In many corrosion-coating systems, the preservation of an oxide layer on the metal surface is crucial to ensure corrosion protection. Frequently, these oxide layers were maintained through the use of chromates and other environmentally harmful substances. Intrinsically conducting polymers have been found to passivate and protect metals via the formation of an oxide layer on the metal surface. Any uncovered area of the metal is passivated by the coating due to the conductive property of the intrinsically conducting polymers (ICP). Testing on polyaniline/ICP systems has shown great potential [32].

Recent examination is being directed toward new corrosion coating technology concerning an interesting material called electroactive conducting polymers (ECP). Since ECPs offer similar properties as harmful chromate coating systems, they may offer a potential alternative in corrosion coating protection. Similar to chromate, ECPs have positive equilibrium potentials relative to iron and aluminum. Tests have shown successful corrosion protection of aluminum alloy by polyaniline and polypyrrole when exposed to sodium chloride solution. However, more exploration is needed to fully understand ECPs and if they offer advantages in corrosion protection [94].

Inorganic sol-gel coatings exhibit desirable barrier properties but cannot be used in conjunction with aluminum alloys or magnesium alloys due to necessary high curing temperatures. Inorganic-organic hybrid sol-gel coatings appear to offer encouraging results in terms of corrosion protection, flexibility, thickness, and curing temperature [95]. The ability of the hybrid sol-gel coating to prevent corrosion is directly related to its barrier properties. Any location where the electrolyte is able to reach the surface of the metal through defects in the coating is likely to result in localized corrosion. The development of coatings able to self-repair these defects is desirable. Self-repairing coatings made up of nanocontainers with the capability of controlled release of encapsulated inhibitor may develop into a new category of self-healing coatings. Unlike many other systems which constantly release small amounts of inhibitor independent of whether damage is present or not, the self-repairing system works by eliciting the release of corrosion inhibitors upon corrosion or damage to the coating, only in this manner is the corrosion inhibitor released. This improved release control, cuts down on inhibitor waste, and improves the durability of the coating. Research has focused on the use of triazole and thiazole derivatives as inhibitors [95]. Improvement in the encapsulation process and control of the inhibitor release is dependent on advancement in nanoreservoir production. As this technology advances, the incorporation of multiple active functions within each coating may be achievable [96]. An example of a self-healing hybrid sol-gel coating combines nanocontainers containing benzotriazole that are impregnated in a sol-gel film. Combining nanocontainers within the hybrid sol-gel film results in prolonged corrosion protection due to the self-healing ability. Furthermore, since the inhibitor is being contained within the nanocontainer, there is no negative

reaction between the inhibitor and the hybrid sol-gel coating that would cause a negative impact on the barrier properties or inhibitor effectiveness [97]. Another organic-inorganic hybrid coating uses a SiO_2 -methacrylate matrix and TiO_2 - CeO_2 nanoparticles. It is presumed that the employment of a binary powder would improve corrosion resistance in two ways, first the even distribution of these nanoparticles throughout the coating should result in desirable barrier properties and secondly the cerium oxide will act as a corrosion inhibitor [95]. The organic-inorganic hybrid coating is only one part of the corrosion protection system; it is necessary to cover it with an additional paint layer. The resulting system has been found to provide good corrosion protection.

New advancements in nanotechnology offer new ideas for developing sophisticated corrosion prevention coating systems. Lvov et al. proposed some new designs of self-healing anti-corrosion coating systems with the addition of nanocontainers equipped with corrosion inhibitors. Upon mechanical damage or initiation of the corrosion process, these nanocontainers release the encapsulated inhibitor directly into the damaged area. This system was tested by loading halloysite nanotubes with the inhibitor benzotriazole and incorporated it into a ZrO_2 - SiO_2 sol-gel coating then deposited it onto aluminum alloy. It was demonstrated after exposure to sodium chloride solution, the anticorrosion efficiency increased and a self-healing effect was obtained. More investigation is needed to determine the fine details of the applicability of this nanotechnology. **Figure 7** displays TEM and SEM images of halloysite nanotubes coatings [98].

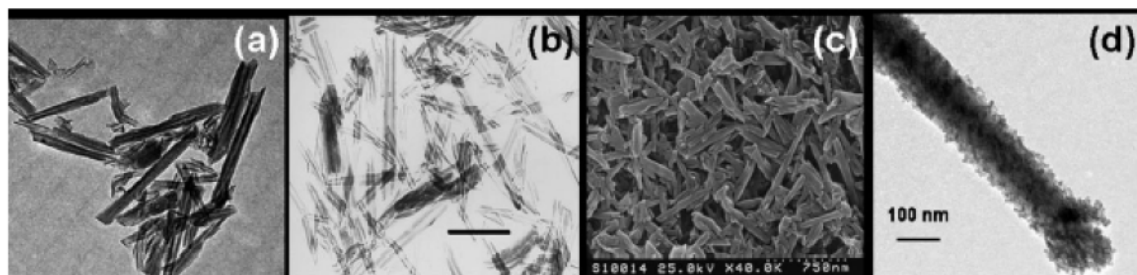


Figure 7. (a, b) TEM images of halloysite nanotubes dispersed in water . (c) SEM image of layer-by-layer nanocoating with $(\text{PEI}/\text{halloysite})_3$ multilayer (top view), and (d) halloysite nanotube coated with $\text{PEI}/\text{PSS} + (\text{PEI}/ 7 \text{ nm silica})_2$ shell.

A recent patent uses similar principles to those of the self-healing coatings, which consists of a coating with evenly distributed microcapsules that contain inhibitors, a film forming compound, and an indicator. Upon breakdown of the microcapsule shell due to the presence of acidic or basic conditions, the contained components are released. There are two types of indicators that could be applied. The first type, exhibits a color change based on pH such as phenolphthalein and the second type, fluoresces in the presence of metal oxidation or formation of a metal ion complex such as 7-hydroxycoumarin or coumarin [99]. Including an indicator would make checking for corrosion much easier. It would aid workers in finding corrosion early and quickly, preventing further damage and decreasing the amount of time needed to inspect vehicles.

Another patent focuses on a coating system that incorporates the corrosion inhibitor molybdenum oxide (MoO_3). The system is comprised of a particulate metal, organic solvent, silane binder with epoxy functional groups, thickener, MoO_3 , water, and potentially a silicate. With all percentages by weight, optimal composition of the system includes particulate metal content of 10 – 40 % with zinc use particularly advantageous, 1 – 30 % organic solvent, 3 – 20 % binder, 0.005 – 2 % thickening agent, 0.5 - 0.7 % or 2 % by weight MoO_3 , water content of 30 – 60 %, 10 % epoxy functional silane, and 0.05 – 5 % silicate. The addition of molybdenum oxide was found to significantly increase corrosion protection when exposed to salt spray [100].

Polysiloxanes have shown promising results in terms of corrosion protection. In testing the acrylated urethane modified polysiloxane, exhibited great durability, film toughness, edge protection, and flexibility. Additionally, the epoxy modified polysiloxane displayed quick adoption of film properties especially in terms of hardness. As a whole, the organically altered polysiloxanes applied for corrosion protection in combination with a zinc rich primer coating show long-term corrosion protection, which is drastically improved compared to the conventional three coat system [101].

A thermoplastic polymeric composition has been developed for corrosion protection and noise dampening of vehicle underbodies and boxed components. This underbody coating and box filler is based on agents that expand upon exposure to heat. Improvements such as decreased weight, greater corrosion protection, boosted mechanical performance, and more significant noise dampening make this a very desirable material with many applications. This material withstands exposure to abrasives such as dust, gravel, or sand as well as those that cause corrosion such as salt, humidity, acidic rain, water, or pollutants at significantly reduced thicknesses than traditional polyvinyl coatings [102].

5.3. Pigment and Binder Focused Coatings

Some commonly used binders are polyurethane binders, epoxy resin-based binders, and alkyd resin-based binders. Polyurethane binders are polymers produced via a reaction between isocyanates and polyols. The type of isocyanate, the addition of hydroxyl, and the ratio of these materials used all play a function in determining the properties of the final polyurethane product. The hydroxyl groups are often polyester or acrylate based and the isocyanates are aromatic or aliphatic. There are also one component polyurethanes based on a polyurethane-isocyanate body that is attached to isocyanate groups. These one-component polyurethanes react with the moisture in the environment, which causes them to cross link and harden. Epoxy resin-based inhibitors are often used for corrosion protection because they provide good chemical stability, adhesion, hardness, flexibility, and toughness. Generally, epoxides are formed by reacting diene with epichlorhydrin that produce glycidyl ethers, which are the main component of the resin. The glycidyl ether based resins are often hardened by reacting them with polyamines or aminoamides. Alkyd resin-based binders are polyesters adapted with carboxylic acids, which are usually used in mild corrosion conditions due to damage to the ester bonds that are relatively common when exposed to atmospheric conditions. They have the greatest chemical stability but are also susceptible to hydrolysis. Testing showed that a two-component epoxy resin hardened with polyamine provided the best corrosion protection followed by a single component polyurethane, and the worst protection was obtained when the alkyd resin was used. The resins were pigmented with iron mica, muscovite, and graphite. Findings showed that iron mica outperformed muscovite and graphite in terms of corrosion prevention. Both synthetic and natural forms of iron mica were used, neither provided corrosion prevention. The use of graphite is also concerning because contact with the surface of the metal substrate could accelerate corrosion. The critical lamellar pigment volume concentration, or concentration of the pigments at which the coating is the most advantageous, were 20% vol for iron mica, 24% vol for muscovite, and 35% vol for graphite [103].

Electrodeposited coatings are commonly used to protect the metal surfaces of vehicles from corrosion. Nearly all vehicles are composed of pieces with sharp, box-like edges, fasteners, or hinges, which are areas vulnerable to corrosion. In order to prevent corrosion within these areas, coating thicknesses have been increased and the pigment content to binder ratio of the coating has been increased. The greater pigment content causes the flow to be restricted while curing but also leads to an undesirable textured film. The textured areas cause greater corrosion due to resultant

micropinholes and voids. Microgels, high molecular weight resins, have been developed that provide similar flow restriction obtained by high pigment content, yet also achieve a smooth surface free of micropinholes and voids. A microgel that achieves this is a cationic microgel, which is created through the interactions between an amine and an epoxy oligomer, that when added to water containing an acid, causes emulsifying, lastly epoxy monomers are added to create the polymer [104].

Another study was performed that focused on the use of pigments and fillers in corrosion resistance paints. The coatings used an epoxy resin binder and were cured using a polyamine hardener. The fillers/pigments were tested and rated based on anticorrosion efficiency, adhesion of the barrier, and inhibition of corrosion at a film thickness of 150 μm . Overall performance showed wollastonite (filler) performed best followed by zinc phosphate (anticorrosion pigment), talc (filler), mixed filler, in order of decreasing effectiveness. Based solely on the physical-mechanical properties, talc (filler) performed the best followed by wollastonite (filler) and hematite (filler). The anticorrosion agent, zinc phosphate, was used as a standard to assess the corrosion protection of the fillers [105]. This study showed that a filler, which provides a balance of both corrosion protection and desirable physical-mechanical properties, must be found for each given application.

The dispersion binder used in a given water-borne coating plays a large role in determining the corrosion protection provided by the coating. The appropriateness of the binder depends upon the size of the polymer particle, more specifically, smaller polymer particles have been found to be more effective than larger particles. However, the mechanical and physical properties of a binder are also very dependent on its size. Research has found that binders consisting of styrene-acrylate or pure acrylate perform much better than vinyl acetate containing binders [106].

The use of pigments composed of a kaolin core and titanium dioxide shell has been found to improve corrosion protection over traditional pigments. Kaolin can be used to provide bulk to the paint product and reduce the amount of higher-priced pigments needed. Testing of the pigments found that optimal corrosion protection and optimal mechanical properties were observed when low concentrations of titanium dioxide were present on the kaolin surface. When using this pigment, the following pigment to binder ratios based on performance from best to worst were $3 > 1.74 > 2.175$ due to alignment of the particle shapes creating a homogeneous film. Unlike regular pigments, the titanium oxide shelled kaolin pigments are anticorrosive and can be used in varying materials at most pH values [107].

An additional pigment with both barrier and anticorrosion properties is spinel MZF pigment. It is prepared by heating the oxidized solid molten phase of micaceous iron oxide to 600°C, washing it with water, firing the oxidized molten phase at 1100°C, and then undergoing calcination causing crystallization of the chloride components and the formation of spinel MZF pigment. The spinel MZF pigment provides barrier protection as well as chemical passivation. Characteristics that lead to the anticorrosive properties of spinel MZF pigment are its lamellar particle shapes and alkalinity [108].

5.4. Water-Rejection/Self-Cleaning

Self-cleaning coatings that reject water have been developed. These coatings consist of a sol-gel coating that self assembles. The coating is fractal and has a super-hydrophobic surface that prevents water saturation. It is also self-cleaning and does so by collecting and washing any materials that have been deposited on the surface of the coating [76].

5.5. Commercial Products

In terms of commercially produced products, the company NOF Metal Coatings Group has developed and commercially produces, GEOBLACK, GEOMET, and GEOKOTE coatings. When the combination of basecoat and topcoat is used in conjunction with one another, high corrosion resistance is provided; matching that expected for chassis components in the automotive industry. Furthermore, they are working on developing a lifetime coating for chassis components. To meet this goal a new product has been produced that is able to obtain thicker coatings. Testing of the new coating has resulted in promising results [109].

Conclusions

Corrosion of metals is becoming increasingly prominent as deicers such as sodium chloride and other highly corrosive chemicals are used on roadways. Developing a high performance, nontoxic, and cost effective corrosion prevention system is very important within the automotive and transportation industries. Numerous research efforts are investigating corrosion mechanisms in order to gain more knowledge to determine effective preventative strategies. Advancements in materials science and nanotechnology have greatly contributed to new and improved highly effective corrosion prevention systems. Along with metallic coatings, polymer and sol-gel coatings show great potential as effective nontoxic alternative low cost coating systems. New innovations such as self-repairing coating systems, capable of successfully protecting metals against corrosion both actively and passively, will become more common when further improvements are made.

References

- [1] Kogler RA, Brydl D, Highsmith C. Recent FHWA experience with metallized coatings for steel bridges. *Mater Performance* 1999; 38: 43-5.
- [2] Akbarinezhad E, Ebrahimi M, Sharif F, Attar MM, Faridi HR. Synthesis and evaluating corrosion protection effects of emeraldine base PANi/clay nanocomposite as a barrier pigment in zinc-rich ethyl silicate primer. *Prog Org Coat* 2011; 70: 39-44.
- [3] Joncoux-Chabrol K, Bonino J-P, Gressier M, Menu M-J, Pebere N. Improvement of barrier properties of a hybrid sol-gel coating by incorporation of synthetic talc-like phyllosilicates for corrosion protection of a carbon steel. *Surface & Coatings Technology*. 2012; 206: 2884-91.
- [4] King AD, Scully JR. Sacrificial Anode-Based Galvanic and Barrier Corrosion Protection of 2024-T351 by a Mg-Rich Primer and Development of Test Methods for Remaining Life Assessment. *Corrosion*. 2011; 67.
- [5] Kirkland NT, Schiller T, Medhekar N, Birbilis N. Exploring graphene as a corrosion protection barrier. *Corros Sci* 2012; 56: 1-4.
- [6] Ordine A, Achete CA, Mattos OR, Margarit ICP, Camargo SS, Hirsch T. Magnetron sputtered SiC coatings as corrosion protection barriers for steels. *Surface & Coatings Technology*. 2000; 133: 583-8.
- [7] Parola S, Verdenelli M, Sigala C, Scharff JP, Velez K, Veytizou C, et al. Sol-gel coatings on non-oxide planar substrates and fibers: A protection barrier against oxidation and corrosion. *J Sol-Gel Sci Technol* 2003; 26: 803-6.

- [8] Schmidt DP, Shaw BA, Sikora E, Shaw WW. Corrosion protection assessment of barrier properties of several zinc-containing coating systems on steel in artificial seawater. *Corrosion*. 2006; 62: 323-39.
- [9] Wang F, Liu J, Li Y, Fan R, Li Y. Complex Barrier Layer of Triazinedithiol Prepared by Electrodeposition and Initiated Polymerization on Aluminum Alloy towards Corrosion Protection. *Int J Electrochem Sci* 2012; 7: 3672-80.
- [10] Weisenburger A, Schroer C, Jianu A, Heinzl A, Konys J, Steiner H, et al. Long term corrosion on T91 and AISI 316L steel in flowing lead alloy and corrosion protection barrier development: Experiments and models. *J Nucl Mater* 2011; 415: 260-9.
- [11] Yasuda HK, Yu QS, Reddy CM, Moffitt CE, Wieliczka DM, Deffeyes JE. "Barrier-adhesion" principle for corrosion protection. *Corrosion*. 2001; 57: 670-9.
- [12] Deflorian F, Fedrizzi L, Bonora PL. Influence of the photo-oxidative degradation on the water barrier and corrosion protection properties of polyester paints. *Corros Sci* 1996; 38: 1697-708.
- [13] Li J, Zhao Y, Hu J, Shu L, Shi X. Anti-icing Performance of a Superhydrophobic PDMS/Modified Nano-silica Hybrid Coating for Insulators. *J Adhes Sci Technol* 2012; 26: 665-79.
- [14] Shi X, Tuan Anh N, Suo Z, Wu J, Gong J, Avci R. Electrochemical and mechanical properties of superhydrophobic aluminum substrates modified with nano-silica and fluorosilane. *Surface & Coatings Technology*. 2012; 206: 3700-13.
- [15] He X, Shi X. Self-repairing coating for corrosion protection of aluminum alloys. *Progress in Organic Coatings*. 2009; 65: 37-43.
- [16] Shi X, Nguyen TA, Suo Z, Liu Y, Avci R. Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating. *Surface & Coatings Technology*. 2009; 204: 237-45.
- [17] Beyer S, Dunkel V, Hasselmann U, Landgrebe R, Speckhardt H. Stress-corrosion in the liquid Zinc phase during high-temperature galvanization of HV screws of strength-10.0 with large dimensions. 2. Experimental-studies and theoretical-studies on damage mechanism and implications for practice. *Materialwiss Werkstofftech* 1994; 25: 459-70.
- [18] Bottcher HJ. Hot galvanization as a means of protection against corrosion in sea-water and in sea-atmosphere. *Metall*. 1968; 22: 1258-&.
- [19] Vollrath K. Hot galvanization for corrosion prevention. *Metall*. 2000; 54: 520-2.
- [20] Barbalat M, Lanarde L, Caron D, Meyer M, Vittonato J, Castillon F, et al. Electrochemical study of the corrosion rate of carbon steel in soil: Evolution with time and determination of residual corrosion rates under cathodic protection. *Corros Sci* 2012; 55: 246-53.
- [21] Diaz B, Swiatowska J, Maurice V, Pisarek M, Seyeux A, Zanna S, et al. Chromium and tantalum oxide nanocoatings prepared by filtered cathodic arc deposition for corrosion protection of carbon steel. *Surface & Coatings Technology*. 2012; 206: 3903-10.
- [22] Wang WH, Yi J, Chen L, Li XY. Numerical Simulation of Transient Process for Corrosion Environment in Coating Crevice with Cathodic Protection. *Journal of Computational and Theoretical Nanoscience*. 2012; 9: 1395-8.
- [23] Liu Y, Shi X. Cathodic protection technologies for reinforced concrete: introduction and recent developments. *Rev Chem Eng* 2009; 25: 339-88.
- [24] Liu Y, Shi X. Modeling cathodic prevention for unconventional concrete in salt-laden environment. *Anti-Corrosion Methods and Materials*. 2012; 59: 121-31.

- [25] Shi X, Fay L, Yang Z, Nguyen TA, Liu Y. Corrosion of deicers to metals in transportation infrastructure: introduction and recent developments. *Corros Rev* 2009; 27: 23-52.
- [26] Chen XB, Birbilis N, Abbott TB. Review of Corrosion-Resistant Conversion Coatings for Magnesium and Its Alloys. *Corrosion*. 2011; 67.
- [27] Presuel-Moreno F, Jakab MA, Tailleart N, Goldman M, Scully JR. Corrosion-resistant metallic coatings. *Materials Today*. 2008; 11: 14-23.
- [28] Podchernyaeva IA, Panasyuk AD, Teplenko MA, Podol'skii VI. Protective coatings on heat-resistant nickel alloys (review). *Powder Metallurgy and Metal Ceramics*. 2000; 39: 434-44.
- [29] Taylor SR, Shiflet GJ, Scully JR, Buchheit RG, VanOoij WJ, Sieradzki K, et al. Increasing the functionality of military coatings using nano-dimensioned materials. *Corrosion Reviews*. 2007; 25: 491-522.
- [30] Tracton AA. *Coatings Materials and Surface Coatings*. Florida: CRC Press; 2006.
- [31] Partnership LTFPTAS. *A Guide to Corrosion Protection for Passenger Car and Light Truck Underbody Structural Components*. Light Truck Frame Project Team Auto/Steel Partnership, 1999.
- [32] Sitaram SP, Stoffer JO, Okeefe TJ. Application of conducting polymers in corrosion protection. *Journal of Coatings Technology*. 1997; 69: 65-&.
- [33] Fujita S, Mizuno D. Corrosion and corrosion test methods of zinc coated steel sheets on automobiles. *Corrosion Science*. 2007; 49: 211-9.
- [34] Huttunen-Saarivirta E, Kuokkala VT, Kokkonen J, Paajanen H. Corrosion behaviour of aircraft coating systems in acetate- and formate-based de-icing chemicals. *Materials and Corrosion-Werkstoffe Und Korrosion*. 2009; 60: 173-91.
- [35] Jones DA. *Principles and Prevention of Corrosion*. New Jersey: Prentice Hall; 1996.
- [36] Gavrilu M, Millet JP, Mazille H, Marchandise D, Cuntz JM. Corrosion behaviour of zinc-nickel coatings, electrodeposited on steel. *Surface & Coatings Technology*. 2000; 123: 164-72.
- [37] Twite RL, Bierwagen GP. Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys. *Progress in Organic Coatings*. 1998; 33: 91-100.
- [38] Zin IM, Howard RL, Badger SJ, Scantlebury JD, Lyon SB. The mode of action of chromate inhibitor in epoxy primer on galvanized steel. *Progress in Organic Coatings*. 1998; 33: 203-10.
- [39] Kendig MW, Buchheit RG. Corrosion inhibition of aluminum and aluminum alloys by soluble chromates, chromate coatings, and chromate-free coatings. *Corrosion*. 2003; 59: 379-400.
- [40] Kalendova A, Vesely D, Stejskal J. Organic coatings containing polyaniline and inorganic pigments as corrosion inhibitors. *Progress in Organic Coatings*. 2008; 62: 105-16.
- [41] Hu R-G, Zhang S, Bu J-F, Lin C-J, Song G-L. Recent progress in corrosion protection of magnesium alloys by organic coatings. *Progress in Organic Coatings*. 2012; 73: 129-41.
- [42] Rammelt U, Reinhard G. APPLICATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) FOR CHARACTERIZING THE CORROSION-PROTECTIVE PERFORMANCE OF ORGANIC COATINGS ON METALS. *Progress in Organic Coatings*. 1992; 21: 205-26.
- [43] Zheludkevich ML, Salvado IM, Ferreira MGS. Sol-gel coatings for corrosion protection of metals. *Journal of Materials Chemistry*. 2005; 15: 5099-111.

- [44] Wang D, Bierwagen GR. Sol-gel coatings on metals for corrosion protection. *Progress in Organic Coatings*. 2009; 64: 327-38.
- [45] Medeliene V, Stankevicius V, Griguševiciene A, Selskiene A, Bikulcius G. The Study of Corrosion and Wear Resistance of Copper Composite Coatings with Inclusions of Carbon Nanomaterials in the Copper Metal Matrix. *Materials Science-Medziagotyra*. 2011; 17: 132-9.
- [46] Mahmoudian MR, Alias Y, Basirun WJ. Effect of narrow diameter polyaniline nanotubes and nanofibers in polyvinyl butyral coating on corrosion protective performance of mild steel. *Progress in Organic Coatings*. 2012; 75: 301-8.
- [47] Arianpouya N, Shishesaz M, Ashrafi A. Analysis of synergistic effect of nanozinc/nanoclay additives on the corrosion performance of zinc-rich polyurethane nanocomposite coatings. *Polymer Composites*. 2012; 33: 1395-402.
- [48] Allahkaram SR, Nazari MH, Mamaghani S, Zarebidaki A. Characterization and corrosion behavior of electroless Ni-P/nano-SiC coating inside the CO₂ containing media in the presence of acetic acid. *Materials & Design*. 2011; 32: 750-5.
- [49] Saji VS, Thomas J. Nanomaterials for corrosion control. *Current Science*. 2007; 92: 51-5.
- [50] Stephenson LD, Kumar A, Bushman J, Phull B. Atmospheric Corrosion Tests of Selected Steel/Coating Materials in Okinawa. *NACE Corrosion Conference and Expo Paper*, 2011. p. 1-15.
- [51] Schuerz S, Fleischanderl M, Luckeneder GH, Preis K, Haunschmied T, Mori G, et al. Corrosion behaviour of Zn-Al-Mg coated steel sheet in sodium chloride-containing environment. *Corrosion Science*. 2009; 51: 2355-63.
- [52] Hosking NC, Strom MA, Shipway PH, Rudd CD. Corrosion resistance of zinc-magnesium coated steel. *Corrosion Science*. 2007; 49: 3669-95.
- [53] Pfeiffer L, Nabbefeld-Arnold E. Zinc magnesium - New metallic coatings for light-gauge steel construction. *Stahlbau*. 2010; 79: 356-62.
- [54] Calle LM, MacDowell LG. 35 Years of Corrosion Protection at the Kennedy Space Center. *KSC Corrosion Technology Laboratory* 2003. p. 1-12.
- [55] Schmidt DP, Shaw BA, Sikora E, Shaw WW, Laliberte LH. Corrosion protection assessment of sacrificial coating systems as a function of exposure time in a marine environment. *Progress in Organic Coatings*. 2006; 57: 352-64.
- [56] Kandi MRS, Shahrabi T, Allahkaram SR, Geramian MA. An investigation on the atmospheric corrosion behaviour of coatings of electrical equipment in the coast of Persian Gulf - Bandar Abbas. *Anti-Corrosion Methods and Materials*. 2004; 51: 209-15.
- [57] Zhang T, Tang D. Current Research Status of Corrosion Resistant Coatings. *Recent Patents on Corrosion Science*. 2009; 1: 1-5.
- [58] Herrasti P, Ocon P. Polypyrrole layers for steel protection. *Applied Surface Science*. 2001; 172: 276-84.
- [59] Hermas AA. Protection of type 430 stainless steel against pitting corrosion by ladder conductive polymer. *Progress in Organic Coatings*. 2008; 61: 95-102.
- [60] Hermas AA, Wu ZX, Nakayama M, Ogura K. Passivation of stainless steel by coating with poly(o-phenylenediamine) conductive polymer. *Journal of the Electrochemical Society*. 2006; 153: B199-B205.

- [61] Wang H, Akid R. Encapsulated cerium nitrate inhibitors to provide high-performance anti-corrosion sol-gel coatings on mild steel. *Corrosion Science*. 2008; 50: 1142-8.
- [62] Delimi A, Galopin E, Coffinier Y, Pisarek M, Boukherroub R, Talhi B, et al. Investigation of the corrosion behavior of carbon steel coated with fluoropolymer thin films. *Surface & Coatings Technology*. 2011; 205: 4011-7.
- [63] Almeida E, Santos D, Uruchurtu J. Corrosion performance of waterborne coatings for structural steel. *Progress in Organic Coatings*. 1999; 37: 131-40.
- [64] Molera P, Oller X, del Valle M, Gonzalez F. Formulation and characterization of anticorrosive paints. *Pigment and Resin Technology*. 2004; 33: 99-104.
- [65] Hernandez LS, del Amo B, Romagnoli R. Accelerated and EIS tests for anticorrosive paints pigmented with ecological pigments. *Anti-Corrosion Methods and Materials*. 1999; 46: 198-204.
- [66] Mahato RR, Jayakrishnan P, Bhattamishra AK, Singh R. Corrosion behaviour of painted HSLA panels in chloride environment a comparative study of different paints. *Anti-Corrosion Methods and Materials*. 2001; 48: 188-93.
- [67] Selvaraj M, Guruviah S. Electrochemical aspects of protection afforded by finish coat on zinc-rich primers. *Pigment and Resin Technology*. 2001; 30: 374-9.
- [68] Gray JE, Luan B. Protective coatings on magnesium and its alloys - a critical review. *Journal of Alloys and Compounds*. 2002; 336: 88-113.
- [69] Kouloumbi N, Tsangaris GM, Mani S, Givalos L. Anticorrosive performance of duplex systems on steel surfaces. *Anti-Corrosion Methods and Materials*. 2000; 47: 156-71.
- [70] Deya M, Vetere V, Romagnoli R, del Amo B. Aluminum tripolyphosphate pigments for anticorrosive paints. *Pigment and Resin Technology*. 2001; 30: 13-24.
- [71] Shashoua Y, Matthiesen H. Protection of iron and steel in large outdoor industrial heritage objects. *Corrosion Engineering, Science and Technology*. 2010; 45: 357-61.
- [72] Schmidt H, Langenfeld S, Nass R. A new corrosion protection coating system for pressure-cast aluminium automotive parts. *Materials & Design*. 1997; 18: 309-13.
- [73] Metroke TL, Kachurina O, Knobbe ET. Spectroscopic and corrosion resistance characterization of GLYMO-TEOS Ormosil coatings for aluminum alloy corrosion inhibition. *Progress in Organic Coatings*. 2002; 44: 295-305.
- [74] Kumar A, Kanta A, Birbilis N, Williams T, Muddle BC. A Pseudoboehmite-Silane Hybrid Coating for Enhanced Corrosion Protection of AA2024-T3. *Journal of the Electrochemical Society*. 2010; 157: C346-C56.
- [75] Zhu D, van Ooij WJ. Corrosion protection of AA 2024-T3 by bis-[3-(triethoxysilyl)propyl]tetrasulfide in neutral sodium chloride solution. Part 1: corrosion of AA 2024-T3. *Corrosion Science*. 2003; 45: 2163-75.
- [76] Taylor SR, Shiflet GA, Scully JR, Buchheit RG, VanOoij WJ, Sieradzki K, et al. Increasing the Functionality of Military Coatings Using Nano-Dimensioned Materials. *ACS Symposium Series*. 2009; 1008 Ch. 8: 126-55.
- [77] Yasakau KA, Zheludkevich ML, Karavai OV, Ferreira MGS. Influence of inhibitor addition on the corrosion protection performance of sol-gel coatings on AA2024. *Progress in Organic Coatings*. 2008; 63: 352-61.

- [78] Khramov AN, Voevodin NN, Balbyshev VN, Donley MS. Hybrid organo-ceramic corrosion protection coatings with encapsulated organic corrosion inhibitors. *Thin Solid Films*. 2004; 447: 549-57.
- [79] Khramov A, Voevodin NN, Balbyshev VN, Mantz RA. Sol-gel-derived corrosion-protective coatings with controllable release of incorporated organic corrosion inhibitors. *Thin Solid Films*. 2005; 483: 191-6.
- [80] Zheludkevich ML, Serra R, Montemor MF, Salvado IMM, Ferreira MGS. Corrosion protective properties of nanostructured sol-gel hybrid coatings to AA2024-T3. *Surface & Coatings Technology*. 2006; 200: 3084-94.
- [81] Voevodin NN, Balbyshev VN, Donley MS. Investigation of corrosion protection performance of sol-gel coatings on AA2024-T3. *Progress in Organic Coatings*. 2005; 52: 28-33.
- [82] Kendig M, Hon M, Warren L. Smart' Corrosion Inhibiting Coatings. *CorrDefense.org* 2003, 1-13 Accessed July 23, 2011 https://www.corrdefense.org/Academia%20Government%20and%20Industry/KeystoneKendigPaper_r6.pdf, 2003.
- [83] Sheffer M, Groysman A, Mandler D. Electrodeposition of sol-gel films on Al for corrosion protection. *Corrosion Science*. 2003; 45: 2893-904.
- [84] Kachurina O, Knobbe E, Metroke TL, Ostrander JW, Kotov NA. Corrosion protection with synergistic LBL/Ormosil nanostructured thin films. *International Journal on Nanotechnology*. 2004; 1: 347-65.
- [85] Beving DE, O'Neill CR, Yan Y. Zeolite Coating System for Corrosion Control to Eliminate Hexavalent Chromium from DOD Applications. *Tri-Service Corrosion Conference*, 2007. p. 1-7.
- [86] Hamdy AS. Enhancing the corrosion resistance of magnesium alloy AZ91D in 3.5 per cent NaCl solution by cerate conversion coatings. *Anti-Corrosion Methods and Materials*. 2006; 53: 367-73.
- [87] Lamaka SV, Montemor MF, Galio AF, Zheludkevich ML, Trindade C, Dick LF, et al. Novel hybrid sol-gel coatings for corrosion protection of AZ31B magnesium alloy. *Electrochimica Acta*. 2008; 53: 4773-83.
- [88] Scharnagl N, Blawert C, Dietzel W. Corrosion protection of magnesium alloy AZ31 by coating with poly(ether imides) (PEI). *Surface & Coatings Technology*. 2009; 203: 1423-8.
- [89] Herdman R, Handy S, Pearson T, Yamamoto T, Ishiwata K, Hara M, et al. Chromium alloy coating with enhanced resistance to corrosion in calcium chloride environments. *US Patent Application*, . No. 20100243463, 2009.
- [90] Legg K. Surface Finishing and Repair Issues for Sustaining New Military Aircraft. *Assets Defense Workshop*, Feb 26-28, 2008. p. 1-9.
- [91] Mosser M, Eddinger K, Fox E. Progress in the Development of Chrome-Free Turbine Engine Coatings, . *Tri-Service Corrosion Conference* 2007. p. 1-31.
- [92] Meng G, Wei L, Zhang T, Shao Y, Wang F, Dong C, et al. Effect of microcrystallization on pitting corrosion of pure aluminium. *Corrosion Science*. 2009; 51: 2151-7.
- [93] Papavinasam S, Attard M, Arseneult B, Revie RW. State-of-the-art of thermal spray coatings for corrosion protection. *Corrosion Reviews*. 2008; 26: 105-45.

- [94] Tallman DE, Spinks G, Dominis A, Wallace GG. Electroactive conducting polymers for corrosion control Part 1. General introduction and a review of non-ferrous metals. *Journal of Solid State Electrochemistry*. 2002; 6: 73-84.
- [95] Zaharescu M, Predoana L, Barau A, Raps D, Gammel F, Rosero-Navarro NC, et al. SiO₂ based hybrid inorganic-organic films doped with TiO₂-CeO₂ nanoparticles for corrosion protection of AA2024 and Mg-AZ31B alloys. *Corrosion Science*. 2009; 51: 1998-2005.
- [96] Shchukin DG, Moehwald H. Self-repairing coatings containing active nanoreservoirs. *Small*. 2007; 3: 926-43.
- [97] Zheludkevich ML, Shchukin DG, Yasakau KA, Moehwald H, Ferreira MGS. Anticorrosion coatings with self-healing effect based on nanocontainers impregnated with corrosion inhibitor. *Chemistry of Materials*. 2007; 19: 402-11.
- [98] Lvov YM, Shchukin DG, Moehwald H, Price RR. Halloysite clay nanotubes for controlled release of protective agents. *Acs Nano*. 2008; 2: 814-20.
- [99] Calle LM, Li W. Coatings and Methods for Corrosion Detection and/or Reduction. US Patent Application, 2010.
- [100] Maze E, Mocquery C, Millet B, Espinosa AFI. Use of MOO₃ as Corrosion Inhibitor, and Coating Composition Containing Such an Inhibitor. In: Application USP, editor. No. 10/416,375, 2001.
- [101] Andrews AF. POLYSILOXANE TOPCOATS – PRODUCT CHOICE FOR OPTIMUM PERFORMANCE. Qstol Protective Coatings: http://www.qstolpaint.com.cn/pc/PdfFiles/polysiloxane_topcoats_AFA.pdf. Accessed June 2, 2011.; 2011.
- [102] Tomalino M, Bianchini G. Heat-expandable microspheres for car protection production. *Progress in Organic Coatings*. 1997; 32: 17-24.
- [103] Kalendova A. Effects of non-isometric pigment particles in organic coatings for corrosion protection. *Pigment and Resin Technology*. 2000; 29: 288-97.
- [104] Sample C. High Edge Coverage Electrocoat Development for Enhanced Corrosion Protection. Tri-Service Corrosion Conference. Denver, CO, 2007. p. 1-8.
- [105] Kalendova A, Vesely D, Kalenda P. A study of the effects of pigments and fillers on the properties of anticorrosive paints. *Pigment and Resin Technology*. 2006; 35: 83-94.
- [106] Kalenda P. Application of water-borne binders to anticorrosive coatings. *Pigment and Resin Technology*. 2002; 31: 357-64.
- [107] Ahmed N, Selim M. Innovative titanium dioxide-kaolin mixed pigments performance in anticorrosive paints. *Pigment and Resin Technology*. 2011; 40: 4-16.
- [108] Emira H. A novel approach to the synthesis of a non-toxic, platy pigment for anticorrosive paints. *Pigment and Resin Technology*. 2005; 34: 132-8.
- [109] Europe NMC. NOF Metal Coatings' R&D Develops GEOMET® Zinc Flake Technology for Corrosion Protection. *Special Chem* 2011.

Chapter 5. Corrosion Inhibitors for Metals in Maintenance Equipment

1. Introduction

Iron, steel, aluminum and aluminum alloys are widely used in maintenance and vehicles used by transportation agencies, which are often at the risk of corrosion associated economic loss [1]. There are several methods available to prevent or protect metals from corrosion, such as barrier protection [2-16], galvanization [17-19], and cathodic protection [20-25]. Among these methods of corrosion prevention and mitigation, the use of corrosion inhibitors is one of the popular treatments [26-29]. Corrosion inhibitors, as defined by International Organization for Standardization (ISO) [30], are 'compounds that when present in a corrosive system at a sufficient concentration, decrease the corrosion rate of metals without significantly changing the concentration of any of the corrosive reagents'. Corrosion inhibitors can cause changes in the state of the protected metal surface through adsorption or formation of compounds with metallic cations. This results in a reduction of the exposed surface area of the metal and an increase in the activation energy of the corrosion processes. The adsorption and formation of protective layers on metals is greatly dependent on both the ability of the inhibitor and metal surface to form chemical bonds and the charges of the surface and inhibitor [31]. The inhibition mechanism of various inhibitors has been proposed [32-43]. Generally corrosion process includes anodic reaction and cathodic reaction, and the addition of corrosion inhibitors can retard the corrosion rate by affecting the two corrosion reactions.

Currently, chromate inhibitors demonstrate the highest corrosion inhibitor performance but are toxic and harmful to the environment [44-50]. Recent research has focused on creating non-toxic oxyanions for use as corrosion inhibitors [51-54]. Some of these compounds include molybdates [55-62], organic thioglycolates [63] and phosphonates [64-66] whereas some inorganic compounds include phosphates, borates, silicates [67-71], and rare earth metal salts [72-79]. Inhibitors can be incorporated into coating systems, in which the coating typically contains a physical barrier layer and an inhibitor layer that physically and chemically suppresses the corrosion processes, respectively.

The aim of this review is to examine the state of the corrosion inhibitors for the protection of various metals/alloys commonly used in maintenance equipment and vehicles, and to identify cost effective, high-performance corrosion inhibitors that may contribute to the preservation of equipment assets.

2. Corrosion Inhibitors Impact on Metals

Inhibitors can be used on a wide variety of metal substrates, and the following sections present a detailed account of inhibitors for iron, steel, aluminum and aluminum alloys, respectively. The focus is placed on the metallic corrosion induced or aggravated by chlorides at ambient temperature and pressure, and near neutral pH (6-8).

2.1. Iron:

Iron metal is inexpensive and strong, which makes it one of the most commonly used metals. Automobiles contain various components made of iron such as the engine cylinder block, crankshaft, and camshaft. Since iron metal is susceptible to pitting corrosion and stress corrosion it is necessary to provide anticorrosion protection. The use of zinc ions, tungstate, and nitrite ions in combination was tested for its inhibition of iron exposed to aqueous conditions. The mixture was found to provide good inhibition efficiency. The inhibitor works by forming zinc tungstate that stops the transfer of oxygen, preventing the cathodic reaction from occurring. It is also believed that the tungstate may prevent the anodic reaction. The synergistic effect is due to the formation of a zinc-anion complex that causes the substrate surface to be passivated. The best performing ratio was 10 parts tungstate to 10 parts nitrite to 1 part zinc, with an optimal concentration of 100 ppm tungstate to 100 ppm nitrite

to 10 ppm zinc [80]. Thiophenol was studied as a corrosion inhibitor on metallic iron and was found to be effective due to the interaction of the sulfur lone pairs and vacant metallic orbitals [81].

Much advancement has been introduced in the field of corrosion inhibitors in recent years. It has been found that effective organic inhibitors adsorb on the metal surface creating a protective film. Phosphonic acids were studied using electrochemical techniques and determined to be effective corrosion inhibitors for iron and low alloyed steels in 3% NaCl solution. The polarization resistance is increased which decreases the direct contact of Cl^- anions to the metal surface. **Table 1** contains the polarization parameters and the corrosion rates of various concentrations of PPA and PPPA. According to the polarization parameters the best result is obtained by PPPA with a concentration of 5×10^{-3} M [82].

Table 1: Potentiodynamic polarization parameters for corrosion of iron in 3% NaCl containing different concentrations of PPA and PPPA [82].

	$c / \times 10^4 \text{ mol l}^{-1}$	$E_{\text{corr}}/\text{mV}$	$j_{\text{corr}}/\mu\text{A cm}^{-2}$	$b_a/\text{mV dec}^{-1}$	$b_c/\text{mV dec}^{-1}$	$\text{IE}_p/\%$	$R_p/\Omega\text{cm}^2$	$\text{IE}_R/\%$	Corrosion/mm per year
PPA	0	-551.3	1085.1	131.2	-274.2	-	27.14	-	12.70
	1	-554.3	577.8	156.0	-221.0	46.75	48.81	44.40	6.75
	5	-628.7	299.9	132.4	-390.0	72.36	99.71	72.78	3.56
	10	-627.5	291.7	124.1	-409.7	73.11	105.62	74.30	3.41
	50	-652.8	252.8	125.5	-267.8	76.70	109.92	75.30	2.95
PPPA	0	-551.3	1085.1	131.2	-274.2	-	27.14	-	12.70
	1	-611.8	278.9	118.6	-317.2	74.92	83.01	67.30	3.26
	5	643.3	203.4	80.4	-133.6	81.25	102.03	73.40	2.37
	10	-654.7	220.1	98.5	-206.1	81.37	105.21	74.20	2.57
	50	-727.2	87.9	92.5	-141.1	91.90	222.16	97.78	1.02

2.2. Steel:

Steel is the most widely used metal today and is very common in the automotive industry. It is used in the main structural components of maintenance equipment and vehicles. In the past, chromate inhibitors have proved successful in decreasing the corrosion rate on steels [83-87]. However, new, nontoxic inhibitors have been developed as potential chromate replacements for use on steel, and literature has reported successful protection of steel with such inhibitors [88-92]. This section will identify these inhibitors and describe their corrosion protection performance.

Research has demonstrated the potential benefits of using inhibitors to protect carbon steel from atmospheric corrosion. Atmospheric corrosion exposure testing used an electrolyte consisting of 2 wt % NaCl and 1 wt % Na_2SO_4 . The best performing inhibitors were sodium dihydrogen orthophosphate, sodium benzoate, sodium nitrite, and sodium nitrate. All of which greatly decrease the corrosion rate of steel. Application of 10 or 100 mM for a day of sodium dihydrogen orthophosphate gave the best protection, while sodium benzoate (10, 100, or 1000 mM treatments) and sodium nitrite (100 or 1000 mM treatments) performed similarly, closely followed by sodium nitrate [93]. A follow-up study on the inhibition provided by sodium dihydrogen orthophosphate exposed to 2 wt % NaCl determined that the application of 10 mM solution for one day reduced the corrosion rate of carbon steel from 0.135 mmpy to 0.06 mmpy. The weight loss measurements after 15 days of atmospheric exposure resulted in 0.096 mmpy for untreated and 0.04 mmpy for treated steel samples, respectively. The difference grew even greater after 6 months with weight loss measurements indicating 0.1 mmpy for untreated and 0.032 mmpy for treated steel, respectively [94].

A similar study evaluated the corrosion inhibition provided by sodium dihydrogen orthophosphate, dicyclohexylamine nitrite, and sodium benzoate on carbon steel exposed to wet/dry

cycling or continuous immersion. The wet/dry cycling test exhibited that 10 mM sodium dihydrogen orthophosphate provided the greatest inhibition efficiency with a corrosion rate of steel at 431.8 $\mu\text{m/y}$, followed by 100 mM dicyclohexylamine nitrite with a corrosion rate of 812.8 $\mu\text{m/y}$, then 100 mM sodium benzoate with a corrosion rate of 965.2 $\mu\text{m/y}$, and lastly the untreated sample exhibited a corrosion rate of 1524 $\mu\text{m/y}$. Over the various wet-dry cycles (shown in **Table 2**), the 10 mM sodium dihydrogen orthophosphate treatment reduced the corrosion rate by an average of 70%. When the same inhibitors and concentrations were tested in immersion exposure, the performance of 10 mM dihydrogen orthophosphate gradually diminished for unknown reason (shown in **Table 3**). However, the higher corrosion rates obtained with the cyclic testing were found to better match corrosion rates found in field testing [95].

Table 2: Inhibitor efficiency under wet/dry cycling conditions [95].

W/D cycle	100 mM SOB Effectiveness (%)	100 mM DICHAN Effectiveness (%)	10 mM SODHOP Effectiveness (%)
0	33.8	33.8	66.2
1	41.0	41.0	70.5
10	62.0	71.7	84.1
20	42.7	35.3	68.3
30	52.3	51.2	65.9
60	31.7	49.1	74.6

Notes: W/D, wet/dry; control, untreated; SOB, sodium benzoate; DICHAN, dicyclohexylamine nitrite; SODHOP, sodium dihydrogen orthophosphate; effectiveness (%) = $[\text{CR}(\text{C}), \text{CR}(\text{IT})] \times 100/\text{CR}(\text{C})$; CR, corrosion rate; C, control; IT, inhibitor treated

Table 3: Inhibitor efficiency under continuous immersion conditions [95].

Days	100 mM SOB Effectiveness (%)	100 mM DICHAN Effectiveness (%)	10 mM SODHOP Effectiveness (%)
0	42.5	42.5	63.0
1	28.5	43.9	30.8
10	55.2	64.1	33.6
20	38.7	38.7	24.5
30	46.8	40.4	18.0

Notes: W/D, wet/dry; control, untreated; SOB, sodium benzoate; DICHAN, dicyclohexylamine nitrite; SODHOP, sodium dihydrogen orthophosphate; effectiveness (%) = $[\text{CR}(\text{C}), \text{CR}(\text{IT})] \times 100/\text{CR}(\text{C})$; CR, corrosion rate; C, Control; IT, inhibitor treated

Rajendran et al. [96] tested the corrosion inhibition ability of a 2-carboxyethyl phosphonic acid (2-CEPA) – Zn^{2+} system and an ethyl phosphonic acid (EPA) – Zn^{2+} system for steel exposed to 60 ppm Cl^- at neutral pH. The 2-CEPA – Zn^{2+} provided an outstanding inhibition efficiency of 98% at 200 ppm, relative to an inhibition efficiency of 58% provided by EPA- Zn^{2+} at 200 ppm. The better inhibition was attributed to a greater concentration of the Fe^{2+} - CEPA complex on the metal substrate, relative to that of the Fe^{2+} - EPA complex. The protective films consisting Fe^{2+} - CEPA and Fe^{2+} - EPA complexes respectively were found to dissolve over time, resulting in decreased ability to inhibit

corrosion. It was found that the systems inhibited both the anodic and cathodic corrosion reactions. An earlier study by the authors [97] found that the EPA-Zn²⁺ system at 300 ppm provided an inhibition efficiency of 88% for steel in 60 ppm Cl⁻. The better inhibition may be attributed to a greater concentration of Zn(OH)₂ in addition to the Fe²⁺-EPA and iron oxides.

An additional study [98, 99] focused on the corrosion inhibition of mild steel exposed to an aqueous solution with a concentration of 60 ppm Cl⁻ provided by amino (trimethylene phosphonic acid) (ATMP), molybdate, and Zn²⁺. Testing of the three inhibitors found that none by itself provided much inhibition (Zn²⁺ actually accelerated corrosion), nor did any combinations of two except for Zn²⁺ and molybdate, which reached an inhibition efficiency of 90%. Combining all three was found to provide the best inhibition, with an optimal mixture concentration of 50 ppm ATMP, 50 ppm Zn²⁺, and 300 ppm molybdate. The aforementioned mixture was able to provide 96% inhibition efficiency and limit the corrosion rate to 0.62 mdd due to the formation of a protective film consisting ZnMoO₄, Fe²⁺-ATMP, Fe₂(MoO₄)₃, and Zn(OH)₂.

Another synergistic approach to corrosion inhibition of carbon steel was investigated by the use of tertiary butyl phosphonate (TBP), zinc ions, and citrate [100]. The ternary formulation of Zn²⁺/TBP/citrate formed a protective film consisting Zn(OH)₂ and Fe²⁺/Fe³⁺-TBP-citrate compounds, reducing the corrosion rate of carbon steel mainly by influencing the cathodic reaction. The ternary formulation was found to be effective in conditions with low chloride concentrations at near neutral pH values (pH 5 to 8). Binary systems containing only Zn²⁺ and TBP were found to be much less effective than the ternary system. The optimal ternary mixture consisting of 50 ppm Zn²⁺, 75 ppm TBP, and 150 ppm citrate was able to reach an inhibition efficiency of 96%.

Similarly, synergistic effects were explored by Rajendran et al. [101] in the corrosion inhibition of mild steel in 60 ppm Cl⁻ with the combination of polyacrylamide (PAA), phenyl phosphonate (PPA), and Zn²⁺. The application of 50 ppm PAA led to an inhibition efficiency of 53%, with a protective film composed of Fe²⁺-PAA and iron oxides. Adding 50 ppm Zn²⁺ to the 50 ppm PAA only increased inhibition efficiency to 65%, with a protective film matching that of the 50 ppm PAA system. Combining the PAA and PPA inhibitors caused an inhibition efficiency of 5%, less than either by itself. The combination of 50 ppm PAA, 300 ppm PPA, and 50 ppm Zn²⁺ provided the best protection with an inhibition efficiency of 95% and corrosion rate of 0.78 mdd. Both anodic and cathodic corrosion reactions were inhibited by the protective film consisting of Fe²⁺-PPA, Fe²⁺-PAA, and Zn(OH)₂. The system composed of 300 ppm PPA and 50 ppm Zn²⁺ provided close to as much protection as the best performing system, with a 95% inhibition efficiency. An early study by the authors [102] found that the 300 ppm PPA - 50 ppm Zn²⁺ system resulted in the highest inhibition efficiency of 95%. The reduction in inhibition efficiency at greater Zn²⁺ concentrations was due to the formation of Zn²⁺ - PPA compound, which in turn slows its diffusion to the substrate surface.

Alternatively, a 1-hydroxyethane-1, 1-diphosphonic acid (HEDP)-Zn²⁺ complex has also been examined by Rajendran et al. [103] for its ability to inhibit corrosion of mild steel in the presence of low chloride concentrations. HEDP is a corrosion inhibitor that has been frequently used and when used in conjunction with Zn²⁺, synergistic inhibition is achieved. The combination of 50 ppm HEDP and 50 ppm Zn²⁺ was found to provide a corrosion inhibition efficiency of 98%. Furthermore, adding additional HEDP or Zn²⁺ was not found to alter the inhibition efficiency of the system. This corrosion protection was attributed to a protective film composed of Fe²⁺-HEDP and Zn(OH)₂ [103]. Similarly, the authors [103] tested the cationic surfactant N-cetyl-N, N, N-trimethyl ammonium bromide (CTAB) was tested for its impact on the inhibition provided by a calcium gluconate (CG) - Zn²⁺ system to the corrosion of mild steel exposed to 60 ppm Cl⁻ at a neutral pH. The 200 ppm CG - 50 ppm Zn²⁺ system was found to have an inhibition efficiency of 86%. The addition of CTAB at a concentration between 25 and 250 ppm was found to raise the inhibition efficiency to 97-98% after five days of exposure. This protection improvement is due to the formation of a film composed of Fe²⁺-CG, Fe²⁺-CTAB, and Zn(OH)₂.

Abdallah et al. [104] proposed the use of sodium salts and derivatives of Neville-Winter acid azo dyes as corrosion inhibitors for carbon steel. The corrosion inhibition of sodium molybdate, tungstate, and monovanadate was observed when exposed to 3.5% sodium chloride solution, respectively. It was found that both the sodium salts and the derivatives could inhibit corrosion by adsorbing to the metal substrate and forming a film, following the Freundlich adsorption isotherm. Protection is believed to be provided by the anions (MoO_4^{2-} , WO_4^{2-} , VO_3^-) reacting with metal cations to form an insoluble salt and thus suppress chloride ion penetration. The insoluble compounds formed from the Neville-Winter acid azo dye derivatives and metal cations also lead to inhibition. The inhibition efficiency increased as the concentration of inhibitor increased.

An additional study [105] on molybdate and tungstate inhibition of corrosion to carbon steel was performed, which found both of them were efficient inhibitors. Iodate was added to molybdate or tungstate as an oxidizing agent and was found to provide synergistic protection. Using an oxidant can allow the amount of necessary inhibitor to be reduced and thus decrease the pH change and scale deposition associated with the inhibitor addition. An insufficient amount of oxidant actually increased the rate of corrosion, confirming that using the proper ratio of concentrations is critical. An early study [106] looked into the inhibition of calcium gluconate and sodium molybdate on carbon steel; both inhibitors are non-toxic and inexpensive. When calcium gluconate is used by itself, it often suffers from dissolution of gluconate from the substrate surface. The combined use of calcium gluconate and sodium molybdate prevents such dissolution and synergistically provides corrosion inhibition. It was also found that increasing the concentration of one of the inhibitors allowed the other to be reduced without ill effects. For example, the combination of 150 ppm sodium molybdate and 50 ppm calcium gluconate, or of 50 ppm sodium molybdate and 150 ppm calcium gluconate, or 200 ppm sodium molybdate and 200 ppm calcium gluconate all provided an inhibition efficiency of approximately 97%.

Organic compounds are commonly used as corrosion inhibitors. The ability of N-coco-amine-2-propionic acid ($\text{C}_{14}\text{H}_{29}\text{N}(\text{C}_2\text{H}_4\text{COOH})_2$) to inhibit corrosion of mild steel exposed to 5% NaCl at pH 6.5 was tested [107]. This compound is a tertiary amine with two carboxylic acid groups. The inhibitor was tested on steel samples that had been pre-corroded, and the 10 ppm inhibitor concentration was found to be the most effective. It was determined that the more significant the corrosion before application of the inhibitor, the lower the inhibition efficiencies. The inhibitor provided inhibition efficiencies above 90%, depending on the amount of pre-corrosion, and that value dropped after an hour of exposure. The protection is the result of inhibitor being adsorbed to the anodic sites of the substrate surface, preventing Fe^{2+} from diffusing away from the surface. Some pitting corrosion occurred, likely due to incomplete coverage of anodic sites by the inhibitor. Another study [108] focused on the corrosion inhibition of tertiary and quaternary amines on mild steel. A tertiary amine with two carboxylic acid groups ($\text{C}_{14}\text{H}_{29}\text{N}(\text{C}_2\text{H}_4\text{COOH})_2$), a tertiary amine with one carboxylic acid group ($((\text{C}_{14}\text{H}_{29})\text{N}(\text{CH}_3)(\text{C}_2\text{H}_4\text{COOH}))$), and two quaternary amines, $[\text{CH}_3(\text{CH}_2)_{15}](\text{CH}_3)_3\text{N}^+\text{Br}^-$ and $\text{C}_{14}\text{H}_{29}\text{N}^+(\text{C}_2\text{H}_6)(\text{C}_6\text{H}_5)\text{Cl}^-$ were tested. The tertiary amines acted as anodic inhibitors. At a pH of 6.5 the surface of the metal substrate was mainly positively charged, causing the tertiary inhibitors to be more effective than the quaternary due to their negatively charged constituents (COO^-). The quaternary inhibitors were however found to be more effective than the tertiary inhibitors at low pH values due to an abundance of positive charges on the substrate surface. In addition to amines, other organic compounds have been tested as potential corrosion inhibitors. Five compounds were studied on steel exposed to two NaCl solution, respectively, namely 3-amino-1,2,4-triazole (3-ATA), 2-amino-1,3,4-thiadiazole (2-ADTA), 5-*p*-tolyl-1,3,4-triazole (TTA), 3-amino-5-methylmercapto-1,2,4-triazole (3-AMTA), and 2-aminobenzimidazole (2-ABA) [109]. It was found that 2-ABA provided the best inhibition, with an inhibition efficiency of 88% in the 2.5% NaCl solution and 94% in the 3.5% NaCl solution. The diazole and triazole derivatives overall were found to be mediocre at inhibiting corrosion of the steel. The inhibition was also found to be related to the shape of the compound, with planar molecules providing better protection. Furthermore,

the corrosion inhibition of phosphonocarboxylic acid salts (PCAS) and fatty amines (FA) to carbon steel exposed to 200 mg/L NaCl solution were explored [110]. The FA inhibited both the anodic and cathodic corrosion reactions and the PCAS inhibited the anodic reaction. When used alone FA provided high inhibition efficiencies at much lower concentrations than those required for PCAS. Adding FA to solutions containing low concentrations of PCAS in solution was found to be effective. The most effective mixture, however, consisted of 200 mg/L PCAS and 50 mg/L FA, attributable to cooperative adsorption of the compounds to the substrate surface. The combination of inhibitors is biodegradable and is non-toxic, enabling its potential widespread use.

Stress corrosion cracking (SCC) is a common failure mode of stainless steels, therefore inhibitors for SCC are desirable. Benzotriazole has been successful in protecting copper and other metals from corrosion. Benzotriazole was tested for its ability to inhibit SCC of 316 stainless steel exposed to 3.4% NaCl and various concentrations of thiosulfate [111]. As the concentration of benzotriazole was increased, its addition was found to reduce SCC, increase the time to failure ratio, and increase the stress ratio. At greater concentrations, benzotriazole was found to influence the morphology of fractures from brittle transgranular to a ductile collapse. The protection is provided through inhibitor adsorption to the substrate surface, which blocks the anodic reaction and associated dissolution.

Although organic compounds have shown good inhibition properties for general corrosion or SCC, there is much less research in developing or evaluating organic inhibitors for pitting corrosion. Wei et al. [112] focused on the pitting inhibition of stainless steel by N-lauroylsarcosine sodium salt (NLS). The 304 stainless steel was exposed to 0.1 M NaCl solution with a neutral pH. The results indicated that the concentration of NLS played a very large role in the inhibition efficiency. The concentration of 30 mM was found to provide total inhibition, via adsorption of the NLS to the metal substrate at significant density. The stainless steel surface is negative in the presence of chloride ions at neutral pH and the adsorption of NLS only enhances the negative characteristic. It is believed that inhibition is the result of the negatively changed NLS layer causing a blocking effect for aggressive anions such as Cl^- .

Lastly, polymers offer environmentally-safe and cost-effective alternatives as corrosion inhibitors. Cation polymers exhibit high corrosion inhibition performance and show great potential when incorporated into paint systems [113]. Specifically, corrosion inhibitors poly-o-aminophenol (PoAP), poly-o-aminothiophenol (PoAT), poly-m-anisidine (PmAS), and polyaniline were evaluated on steel exposed to artificial sea water. As shown in **Table 4**, a concentration of these polymers at 0.5% and 1% both significantly decreased the corrosion rate of the steel. This is likely due to a chelating effect, which induces corrosion inhibition. Additionally, the polyamines were introduced into paint formulations and found to have good adhesion and outstanding corrosion inhibition properties.

Table 4. Corrosion rate of steel in the presence of polymers as corrosion inhibitors [113].

Product Polymer	Conc. of the Corrosion Inhibitor = 0.5%		Conc. of the Corrosion Inhibitor = 1%	
	Av. Wt. Loss (gm)	Corrosion Rate $\times 10^2$ $\text{mg/cm}^2 \cdot \text{day}$	Av. Wt. Loss (gm)	Corrosion Rate $\times 10^2$ $\text{mg/cm}^2 \cdot \text{day}$
Blank	0.0161	58.57	0.0160	57.15
Polyaniline	0.0125	44.64	0.0083	29.64
PoAP	0.0124	44.28	0.0082	28.30
PoAT	0.0137	48.92	0.0077	27.50
PmAS	0.0095	33.92	0.0076	26.14

Table 5 summaries the performance of the previously discussed inhibitors on steel. It is rather difficult to compare these inhibitors, as each test consisted of various concentrations of an electrolyte and exposure times were variable. Note that the corrosion rates measured were averaged across steel coupons and/or averaged over time and thus only provide a relative reference. The corrosion of steel in maintenance equipment can often occur in a localized manner; as such, the corrosion-induced deterioration tends to progress at a rate much faster than implied by the average corrosion rates shown in **Table 5**.

Table 5. Comparison of inhibitor test results for steels.

Compound Tested	Concentration	Test Method	Results	Corrosion Rate (mm/year)	Ref.
sodium dihydrogen orthophosphate	10 mM	Exposure to 2% NaCl solution for one day. Ave. Wt. Loss Measurement	Treated 0.06 mm/y Untreated 0.135 mm/y	--	[93]
sodium dihydrogen orthophosphate	10 mM	Immersion in 2 % NaCl and 1% Na ₂ SO ₄ for 30 days	0.3912 mm/y	--	[95]
dicyclohexylamine nitrite	100 mM	Immersion in 2 % NaCl and 1% Na ₂ SO ₄ for 30 days	0.2845 mm/y	--	[95]
sodium benzoate	100 mM	Immersion in 2 % NaCl and 1% Na ₂ SO ₄ for 30 days	0.254 mm/y		[95]
2-carboxyethyl phosphonic acid (2 CEPA) – Zn ²⁺	200 ppm (2-CEPA) 50 ppm Zn ²⁺	Immersion test in 60 ppm Cl ⁻ solution	Weight Loss Method 98 % Inhibitor Efficiency	--	[96]
ATMP-MoO ₄ ²⁻ -Zn ²⁺	50 ppm ATMP 50 ppm Zn ²⁺ 300 ppm MoO ₄ ²⁻	Immersion test in 60 ppm Cl ⁻ solution	Weight Loss Method 96 % Inhibitor Efficiency Corr. Rate 0.62 mdd	0.0029	[97]
Zn ²⁺ /TBP/Citrate	50 ppm Zn ²⁺ 75 ppm TBP 150 ppm Citrate	Immersion test in 60 ppm Cl ⁻ solution for 7 days	Weight Loss Method 96% Inhibitor Efficiency Corr. Rate 0.71 mdd	0.0033	[100]
PAA/PPA/Zn ²⁺	50 ppm PAA 300 ppm PPA 50 ppm Zn ²⁺	Immersion test in 60 ppm Cl ⁻ solution for 7 days	Weight Loss Method 95% Inhibitor Efficiency Corr. Rate 0.72 mdd	0.0033	[101]
HEDP-Zn ²⁺	50 ppm HEDP 50 ppm Zn ²⁺	Immersion test in 60 ppm Cl ⁻ solution	98 % Inhibitor Efficiency	--	[103]
CTAB/CG/Zn ²⁺	25 ppm CTAB 200 ppm CG 50 ppm Zn ²⁺	Immersion test in 60 ppm Cl ⁻ solution for 5 days	98 % Inhibitor Efficiency	--	[103]

Sodium benzoate	100 mM	Tafel and Polarization Tests 180 days exposure	Tafel extrapolation 94% Inhibition Efficiency	--	[109]
2-aminobenzimidazole (2-ABA)	2 x10 ⁻² M	Exposure to 3.5% NaCl solution	Tafel extrapolation 94 % Inhibition Efficiency	--	[109]
polyaniline	1%	Immersion in Artificial Sea Water for 28 days	0.4464 mg/cm ² · day	0.207	[113]
PoAP	1%	Immersion in Artificial Sea Water for 28 days	0.4428 mg/cm ² · day	0.205	[113]
PoAT	1%	Immersion in Artificial Sea Water for 28 days	0.4892 mg/cm ² · day	0.226	[113]
PmAS	1%	Immersion in Artificial Sea Water for 28 days	0.3392 mg/cm ² · day	0.157	[113]

2.3. Aluminum and Aluminum Alloys

Very high strength-weight ratios among other desirable properties, makes aluminum and aluminum alloys versatile materials and extensively used in maintenance equipment and vehicles. In the presence of chlorides, aluminum and aluminum alloys are susceptible to general corrosion, pitting corrosion, granular corrosion, etc. As such, protective systems are necessary to prevent or mitigate such risks. The standard mechanism of corrosion protection works when a dense oxide film forms on the surface of aluminum alloys by exposure to the air. However, if exposed to aggressive chloride ions, Cl⁻ adsorption occurs within the protective film and the accumulation leads to damaging effects of the protective layer. The separation of the intermetallic particles also causes aluminum alloys to become very susceptible to localized corrosion. Pitting corrosion caused by exposure to aggressive chloride medium is a growing concern and a frequent cause of failure.

Mahjani et al. [114] tested Inorganic corrosion inhibitors for their ability to reduce the corrosion of an aluminum alloy exposed to a 0.5 M Na₂SO₄ and 0.2 M NaCl solution. The inorganic inhibitors including: NaNO₂, NaNO₃, Na₂MoO₄, Na₂WO₄, K₂CrO₄, and K₂Cr₂O₇ were tested for their ability to prevent the dissolution of the oxide film on the aluminum alloy surface and the formation of AlCl₃, both of which can lead to pitting corrosion. The results found the following order of inhibition efficiency from greatest to least: CrO₄²⁻, Cr₂O₇²⁻, NO₃⁻, WO₄²⁻, MoO₄²⁻, and NO₂⁻.

The use of organic compounds as corrosion inhibitors has played an important role in the corrosion prevention of aluminum and other metals in highly corrosive environments. Many studies have examined the potential anti-corrosion properties of benzotriazole and its derivatives. Onal and Aksut [115] tested tolyltriazole (TTA) for its ability to control the corrosion of various aluminum alloys exposed to 1M NaCl at a pH of 6. A concentration of 2 mM TTA yielded an inhibition efficiency ranging from 88 – 92 % and a concentration of 20 mM TTA provided 94 – 95 % inhibition efficiency, when applied to the Al - 8% Si - 3% Cu alloy. For the Al - 4% Cu alloy, the inhibition efficiency ranged from 85 – 90 % and 89 – 92 % for TTA concentrations of 2 mM and 20 mM, respectively. TTA provided inhibition efficiencies of 87 – 91 % at 2 mM TTA and 89 – 93 % at 20 mM TTA to the Al – 12% Cu alloy. The Al - 22% Cu - 4% Fe alloy experienced inhibition efficiencies between 88 - 92% at 2 mM TTA and 90 - 95% at 20 mM TTA. These inhibition efficiencies depended on the temperature of the solution. TTA inhibits the cathodic reaction and is less effective as temperature increased from 15 °C to 35 °C. TTA provides corrosion inhibition by

adsorbing onto the Cu of the alloys, causing the formation of a protective Cu(I)-TTA film on the metal surface .

Similarly, Sherif [116] tested the inhibitor 3-amino-5-mercapto-1,2,4-triazole (AMTA) was tested for its ability to inhibit corrosion of aluminum (99.99%) in aerated Arabian Gulf seawater (AGS) and 3.5% NaCl. The AMTA molecules inhibited the general and pitting corrosion of Al in both solutions. A shift towards less negative values of the corrosion and pitting potential of Al and an increased polarization resistance was observed when AMTA is used. The inhibition efficiency for 1 mM AMTA was 70% and for 5 mM was 79% in the NaCl solution. AMTA was adsorbed onto the metallic surface, creating an aluminum oxide compound to prevent the formation of aluminum chlorides that facilitates the corrosion. **Figure 1** is the chemical structure of AMTA and **Table 6** presents the corrosion parameters from potentiodynamic polarization curves and inhibition efficiencies (IE) of the inhibitor at two concentrations. .

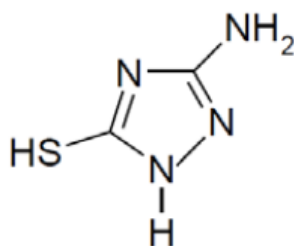


Figure 1. Chemical structure of 3-amino-5-mercapto-1,2,4-triazole (AMTA)

Table 6: Corrosion parameters obtained from potentiodynamic polarization curves for the Al electrode in AGS and 3.5% NaCl solutions in absence and presence of AMTA [116].

Solution	Parameter								
	$E_{Corr}/$ mV	$j_{Corr}/$ $\mu A\ cm^{-2}$	$B_c/$ mV dec ⁻¹	$B_a/$ mV dec ⁻¹	$j_{Pass}/$ $\mu A\ cm^{-2}$	$E_{Pit}/$ mV	$R_p/$ $\Omega\ cm^2$	$K_{Corr}/$ mmy ⁻¹	IE / %
AGS only	-1435	2.5	180	170	4.83	-738	15.22	0.0273	—
+ 10^{-3} M AMTA	-1375	0.5	135	195	3.65	-710	69.38	0.0055	79.8
+ 5×10^{-3} M AMTA	-1340	0.35	105	210	1.28	-685	86.95	0.0038	86.1
3.5% NaCl only	-1485	2.0	140	165	4.52	-735	16.46	0.0218	—
+ 10^{-3} M AMTA	-1395	0.6	105	180	3.14	-725	48.10	0.0065	70.2
+ 5×10^{-3} M AMTA	-1355	0.42	92	207	1.49	-690	65.93	0.0046	78.9

Current research efforts have been focused on creating environmentally safe corrosion inhibitor alternatives. Allachi et al. [117] reported that the use of environmentally friendly $CeCl_3$ (a lanthanide salt) at 1 mM on aluminum alloy AA6060 provided effective corrosion inhibition in the presence of 3.5% NaCl. Generally corrosion would occur at the intermetallic compound α -Al(Fe,Mn)Si, but the precipitation of cerium compounds on these intermetallics reduced the corrosion rate. Cerium chloride was classified as a cathodic inhibitor. Specially the Ce^{2+} precipitates and forms a complex with OH^- , which blocks cathodic sites, consequently decreasing the rate of the corrosion process. **Figure 2** represents a model of the formation of cavities, which occurs during pitting corrosion on aluminum alloys exposed to aggressive chloride ions. The use of $CeCl_3$ effectively suppresses the growth of the pits.

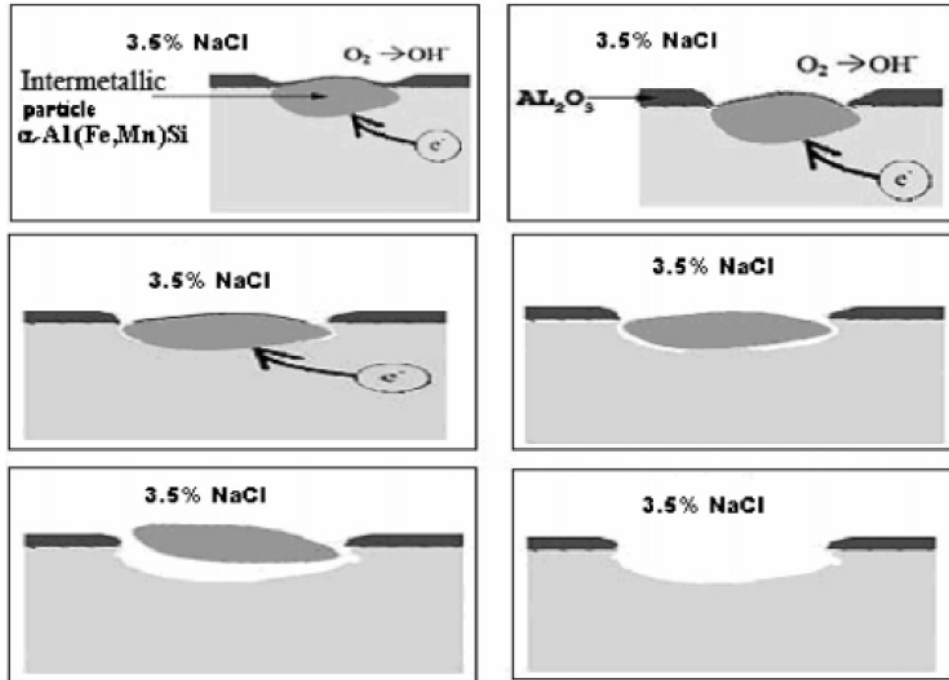


Figure 2. Model of the process of formation of cavities by localized alkaline corrosion.

Accumulative research has confirmed the inhibiting effect of compounds that decrease corrosion rates by forming deposits on the surface of aluminum alloys. Lamaka et al. [118] examined the corrosion inhibiting properties of salicylaldoxime, 8-hydroxyquinoline, and quinaldic acid. Aluminum alloys have a favorable strength to weight ratio making them a very widely used material in the aerospace industry. The presence of the inhibitors caused the formation of a thin adsorptive protective layer on the surface of the alloy. This layer prevents both the dissolution of Mg, Al, and Cu from the active intermetallic sites and the adsorption of chloride ions onto the surface (shown in **Figure 3**). This research provides consistent evidence that organic compounds capable of forming insoluble complexes within intermetallic zones have potential for pitting initiation. These organic inhibitors are believed to be as effective as mercaptobenzothiazole, Ce and La salts. Visual observation shows low corrosion attack on the surface of the samples immersed in an electrolyte solution with 0.05g/L organic inhibitors.

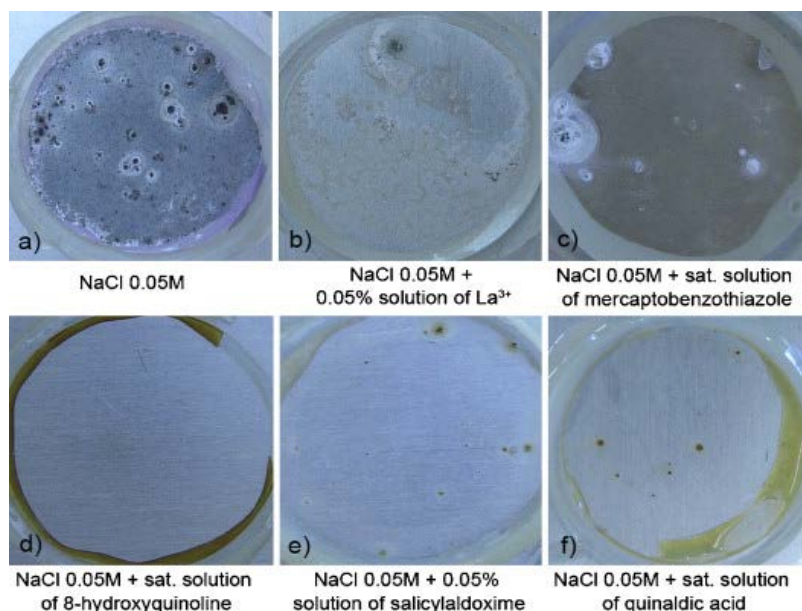


Figure 3: Photos of the AA2024 samples after immersion for 2 weeks in 0.05 M NaCl with or without inhibitors [118].

Inorganic inhibitors are effective partially due to the formation of oxide film on the metal surface, whereas organic inhibitors work by their adsorption on the metallic substrate. Among the most effective inhibitors in neutral pH conditions were benzylic acid, citric acid, and oxalic acid [119]. Bereket and Yurt [119] revealed that hydroxy carboxylic acids were effective corrosion inhibitors for aluminum alloy 7075 exposed to 0.05 M NaCl solution and shifted the pitting corrosion potential to more positive values.

Much attention has been focused on sol-gel coatings as an alternative to chromate coatings for protecting aluminum alloys. Sol-gel coatings offer exceptional adhesion to the substrate and corrosion protection by forming an unreactive layer between the metal and the corrosive environment. However, cracks and micro-pores within the coating make it difficult for these coatings to be effective for extended periods of time. In this context, corrosion inhibitors can be introduced into the sol-gel process to increase the lifetime of the corrosion protection. An organic corrosion inhibitor, chloranil (its chemical structure is shown in **Figure 4**), was used to dope the sol-gel coating applied to 2017 aluminum alloy. It was observed that adding low concentrations of chloranil enhanced the efficiency of the sol-gel coating over long NaCl exposure times [120].

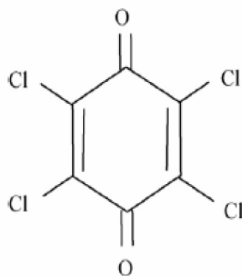


Figure 4. Chemical structure of the tetrachloro-p-benzoquinone (chloranil).

An innovative corrosion inhibitor technique involving nanoparticle based inhibitors exhibits new advantages and shows promising results [121]. The performance of this nanoparticle technology is comparable to chromate-based inhibitors. The corrosion inhibitors remain within the coating until corrosion occurs. The corrosion triggers the release of nanoparticles, which migrate to the metal surface and begin to slow down the corrosion process.

Table 7 summarizes the results of various inhibitors on aluminum and aluminum alloys. It is rather difficult to compare these inhibitors due to the inherent diversity in the test method, electrolyte concentration, etc.

Table 7. Comparison of inhibitor test results for aluminum or aluminum alloy.

Compound Tested	Concentration	Test Method	Results	Ref.
CeCl ₃	10 ⁻³ M	Electrochemical Technique, Immersion in 3.5% NaCl for 30 days	Wt. loss 10 µg/cm ² Inhibition Eff. 80%	[117]
salicylaldoxime	0.05 g/l	Electrochemical Impedance Spec. Immersion in 0.05 M NaCl + Inhibitor solution for approximately 400 hours	Polarization Resist. 9740 kΩcm ²	[118]
8-hydroxyquinoline	0.05 g/l	Electrochemical Impedance Spec. Immersion in 0.05 M NaCl + Inhibitor solution for approximately 400 hours	Polarization Resist. 152.8 kΩcm ²	[118]
quinaldic acid	0.05 g/l	Electrochemical Impedance Spec. Immersion in 0.05 M NaCl + Inhibitor solution for approximately 400 hours	Polarization Resist. 4035 kΩcm ²	[118]
Benzylic acid	10 ⁻² M	Polarization Technique Immersion in 0.05 M NaCl solution for 20 days	E _{pit} -E _{corr} = 335 V	[119]
Citric acid	10 ⁻² M	Polarization Technique Immersion in 0.05 M NaCl solution for 20 days	E _{pit} -E _{corr} = 444	[119]
Oxalic acid	10 ⁻² M	Polarization Technique Immersion in 0.05 M NaCl solution for 20 days	E _{pit} -E _{corr} = 371	[119]
3-amino-5-mercapto-1,2,4-triazole (AMTA)	5 x 10 ⁻³ M	Electrochemical Impedance Spec. Immersion in Arabian Gulf Seawater and 3.5% NaCl solution	Inhibition Eff. Seawater 86.1% 3.5% NaCl 78.9%	[116]
Chloranil doped sol-gel	6 x 10 ⁻⁴ M	Electrochemical Impedance Spec. Immersion in 5% NaCl solution	Polarization Resist. 2.5 x 10 ⁵ ± 8 x 10 ⁴ Ωcm ₂	[120]

3. Rust Converters

Accumulative studies have found that the proper preparation of the metal surface plays a critical role in the lifetime of the coating. This section is dedicated to the use of rust converters for corrosion protection. Rust converters are applied onto corroded metal surfaces and can be considered in the extended family of corrosion inhibitors.

Rust converters are designed to convert existing rust into a protective coating that blocks moisture and prevents or suppresses future corrosion. Rust converters are directly applied to the metal surface and act as a primer when supplemented with paint. Effective use of rust converters is dependent on the given application. Some of the variables that vary greatly with each specific situation include the concentrations and types of chemicals to be included, the application time, and amount of rust converter to be applied. Additionally, the composition of the metal and the exposure environment are both of crucial importance when considering rust converters. Research [122] shows that the use of a rust remover led to better coating adhesion, which increases the performance of coating system and decreases the corrosion rate of the metal substrate.

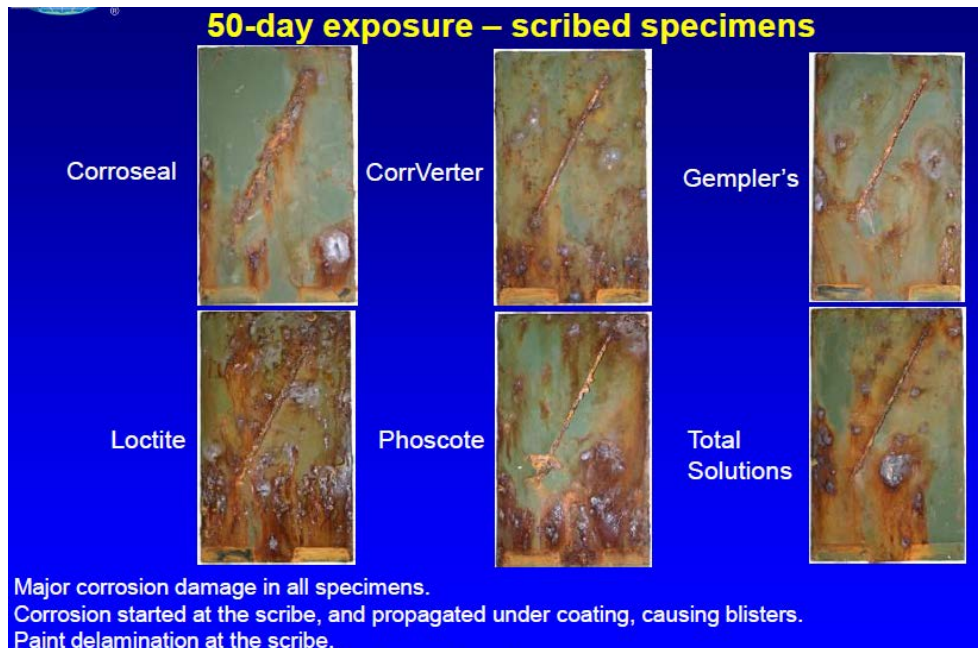
The oxide layer generated on steel surfaces varies by the service environment [123]. In environments without chloride ions, only lepidocrocite and goethite were found in the crystalline corrosion products. In environments with chloride ions, spinel phase and akaganeite were also formed. Iron oxide layers form on the steel surface both in the presence and absence of rust converters. The presence of rust converters compresses the system, causing a change in conductivity. Rust converters containing copper compounds can accelerate magnetite oxidation [124].

Most rust converters are composed of tannic acid, phosphoric acid, or a mixture of both. The solvent used in rust converters has been found to affect their rate of distribution through the rust layer. Alcohols are commonly used as the solvent for rust converters, and high performance is often obtained with a mixture of butyl and ethyl alcohol. A mixture of isopropanol and tertbutanol has also been reported effective [125].

The application time of rust converters depends on the type of metals present. It is difficult to optimize the application time in light of the frequency at which multiple corrosion layers exist and the wide variety of metals present in the rust layers. The conversion and subsequent protection provided by rust converters can vary significantly, depending on the converter, the conditions, and the substrate [125].

In 2003, Bolivar et al. [126] concluded that for each tannic concentration, an optimal combination of alcohol could be used to increase the conversion process on the corroded steel. Additionally, about 90% transformation occurred with non-stoichiometric spinel phase and 30% magnetically blocked goethite was transformed whereas akaganeite is unchanged by the converters.

In 2009, Caseres [127] evaluated the following rust converters in atmospheric exposure: Gempler's TM (water-based, tannic acid), Loctite rust treatment TM (polymeric-based, barium sulfate), Total Solutions TM (water-based, tannic acid), Phoscoat TM (phosphoric acid – current USMC product), VpCI CorrVerter TM (combined rust converter and primer), Corroseal TM (water-based, tannic acid with primer), Gem Rust Killer TM. It was concluded that rust converters were not suitable for damaged coatings as extensive corrosion damage was observed in all of the scribed steel specimens as illustrated in **Figure 5a**. However, visual observation (**Figure 5b**) indicates the best results in the unscribed steel specimens were obtained with Total Solutions TM. Nevertheless, the evaluation was focused on the comparison of macroscopic performance, instead of the underlying protection mechanisms.



(a)

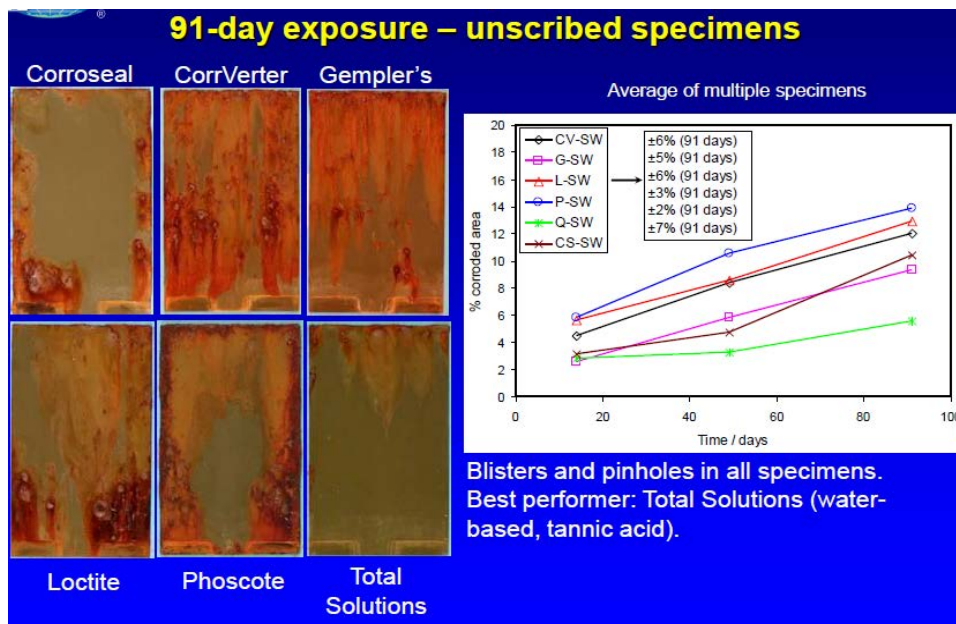


Figure 5(a), Photos of scribed steel specimens treated with various rust converters; (b) Photos and data of unscribed steel specimens, as a function of rust converter, which were adopted from [127].

3. Other Studies of Inhibitors for Chloride Induced Corrosion

Pitting corrosion of metals induced by chloride is a complex problem with significant engineering implications, featuring spatially separated yet electrochemically coupled local anodes and cathodes on the metal surface [128-131]. Although many inhibitors have been developed to prevent or suppress the corrosion process, the mechanism of inhibition by inhibitors is generally poorly understood and difficult to study. In most cases empirical testing provides information as to whether a specific molecule or layer is effective or not for a given substrate in a particular medium. Knowledge about the surface chemistry of coating layer could help to resolve the mechanism of inhibitor action. Recently many surface analytical techniques [132-138], such as X-ray photoelectron spectroscopy

(XPS), scanning electrochemical microscopy (SECM) and atomic force microscopy (AFM), have been developed to investigate the surface properties of coating layer, which can help us understand the corrosion process and optimize inhibitors with the best anti-corrosion performance.

XPS is a suitable method that provides information on chemical bonding at the metal–adsorbate interface, which offers the possibility of distinguishing between different types of chemical bonds of surface atoms on the basis of chemical shift and change in shape of the XPS peaks. Therefore, XPS is a useful tool to investigate the surface chemistry of inhibitors coated on metal surface [132-136]. Finsgar et al. [139, 140] gave a comprehensive surface analysis of pure copper immersed in 3% NaCl solution containing 1-Hydroxybenzotriazole (BTAOH) and Benzotriazole (BTAH) using XPS technique. No cupric species were formed on the copper surface within the treatment time, in either pure 3% NaCl or BTAH- or BTAOH-containing solutions. The analysis of X-ray induced Auger Cu $L_{3}M_{4,5}M_{4,5}$ spectra recorded at grazing angles after treatment in a BTAH-containing solution showed an increase in the specific peak attributed to the formation of the Cu(I)BTA surface complex. This peak was used to clearly differentiate between the Cu(I)BTA complex and cuprous oxide.

SECM technique has been successfully applied to several corrosion problems, such as pitting corrosion [141-144], the galvanic corrosion of zinc-iron [145, 146], mapping of the surface conductivity of passive layers [147, 148], the influence of inhibitors [149-152], and the examination of organic coatings on metallic substrates [145, 152-155]. Izquierdo et al. [152] investigated the film formation of benzotriazole towards corrosion of copper by SECM, which was operated in the feedback mode by using ferrocene–methanol as redox mediator, and the sample was left unbiased at all times to freely attain its open circuit potential in the test environment. Shape changes of the approach curves indicated the inhibitor film formation process, which showed the transition from an active conducting behavior towards ferrocinium reoxidation typical of unprotected copper, to a surface exhibiting insulating characteristics when the metal was covered by a surface film containing the inhibitor.

Atomic force microscopy (AFM) offers nanoscale resolution, particularly for imaging in liquids, and it has been widely used for corrosion research in the past decade. For such applications, AFM provides the nanoscale topographic information of metals in electrolyte that is otherwise difficult to obtain. A wide range of metallic substrates have been studied, including steel [156-160], aluminum alloy [161-165], titanium [166-169], zinc [170-172], nickel [173] etc. John et al. [160] used AFM and neutron reflectometry to investigate the anti-corrosion process of inhibitors comprising cetyl pyridinium chloride (CPC), dodecyl pyridinium chloride (DPC), 1-hydroxyethyl-2-oleic imidazoline (OHEI) and cetyl dimethyl benzyl ammonium chloride (CDMBAC), which were adsorbed on the surface of steel. Corrosion measurements confirmed that maximum inhibition efficiency coincides with the solution critical micelle concentration.

4. Concluding Remarks

Inhibitors are an important tool for corrosion protection of metals commonly used in maintenance equipment and vehicles. A variety of inhibitors show promising results in corrosion protection of iron, steel, aluminum and aluminum alloys, respectively. Numerous compounds have been identified as alternatives to toxic chromate inhibitors. This review focused on the corrosion inhibitors for chloride environments which feature ambient temperature and near-neutral pH. Organic inhibitors offer low cost, low environmental impact, and effective corrosion protection of steel and aluminum while inorganic inhibitors could provide the advantages of enhanced strength, anti-high temperatures, etc. Additionally, a few polymers performed sufficiently as corrosion inhibitors when incorporated into paint systems. There have been limited studies at the microscopic level or in situ to fully understand the behavior and inhibition mechanisms of corrosion inhibitors, as the vast majority of the studies thus far have been conducted at the macroscopic level and ex-situ. It was reported that

synergistic effects can greatly improve the performance of inhibitors, which points to the right direction for current and future developments of corrosion inhibitors. Concentration of inhibitors also plays a vital role in their performance and cost-effectiveness. Therefore, it is crucial that the optimal concentration is used for the selected inhibitors package. The conditions in which the inhibitors will be exposed are also of great importance. Specific inhibitors should be chosen carefully with the application and service environment. There are emerging inhibitor solutions that leverage the advances in nanotechnology, green technology, and smart materials.

References

- [1] Kogler RA, Brydl D, Highsmith C. Recent FHWA experience with metallized coatings for steel bridges. *Mater Performance* 1999; 38: 43-5.
- [2] Akbarinezhad E, Ebrahimi M, Sharif F, Attar MM, Faridi HR. Synthesis and evaluating corrosion protection effects of emeraldine base PANi/clay nanocomposite as a barrier pigment in zinc-rich ethyl silicate primer. *Prog Org Coat* 2011; 70: 39-44.
- [3] Joncoux-Chabrol K, Bonino J-P, Gressier M, Menu M-J, Pebere N. Improvement of barrier properties of a hybrid sol-gel coating by incorporation of synthetic talc-like phyllosilicates for corrosion protection of a carbon steel. *Surface & Coatings Technology*. 2012; 206: 2884-91.
- [4] King AD, Scully JR. Sacrificial Anode-Based Galvanic and Barrier Corrosion Protection of 2024-T351 by a Mg-Rich Primer and Development of Test Methods for Remaining Life Assessment. *Corrosion*. 2011; 67.
- [5] Kirkland NT, Schiller T, Medhekar N, Birbilis N. Exploring graphene as a corrosion protection barrier. *Corros Sci* 2012; 56: 1-4.
- [6] Ordine A, Achete CA, Mattos OR, Margarit ICP, Camargo SS, Hirsch T. Magnetron sputtered SiC coatings as corrosion protection barriers for steels. *Surface & Coatings Technology*. 2000; 133: 583-8.
- [7] Parola S, Verdenelli M, Sigala C, Scharff JP, Velez K, Veytizou C, et al. Sol-gel coatings on non-oxide planar substrates and fibers: A protection barrier against oxidation and corrosion. *J Sol-Gel Sci Technol* 2003; 26: 803-6.
- [8] Schmidt DP, Shaw BA, Sikora E, Shaw WW. Corrosion protection assessment of barrier properties of several zinc-containing coating systems on steel in artificial seawater. *Corrosion*. 2006; 62: 323-39.
- [9] Wang F, Liu J, Li Y, Fan R, Li Y. Complex Barrier Layer of Triazinedithiol Prepared by Electrodeposition and Initiated Polymerization on Aluminum Alloy towards Corrosion Protection. *Int J Electrochem Sci* 2012; 7: 3672-80.
- [10] Weisenburger A, Schroer C, Jianu A, Heinzel A, Konys J, Steiner H, et al. Long term corrosion on T91 and AISI 316L steel in flowing lead alloy and corrosion protection barrier development: Experiments and models. *J Nucl Mater* 2011; 415: 260-9.
- [11] Yasuda HK, Yu QS, Reddy CM, Moffitt CE, Wieliczka DM, Deffeyes JE. "Barrier-adhesion" principle for corrosion protection. *Corrosion*. 2001; 57: 670-9.
- [12] Deflorian F, Fedrizzi L, Bonora PL. Influence of the photo-oxidative degradation on the water barrier and corrosion protection properties of polyester paints. *Corros Sci* 1996; 38: 1697-708.

- [13] Li J, Zhao Y, Hu J, Shu L, Shi X. Anti-icing Performance of a Superhydrophobic PDMS/Modified Nano-silica Hybrid Coating for Insulators. *J Adhes Sci Technol* 2012; 26: 665-79.
- [14] Shi X, Tuan Anh N, Suo Z, Wu J, Gong J, Avci R. Electrochemical and mechanical properties of superhydrophobic aluminum substrates modified with nano-silica and fluorosilane. *Surface & Coatings Technology*. 2012; 206: 3700-13.
- [15] He X, Shi X. Self-repairing coating for corrosion protection of aluminum alloys. *Prog Org Coat* 2009; 65: 37-43.
- [16] Shi X, Nguyen TA, Suo Z, Liu Y, Avci R. Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating. *Surface & Coatings Technology*. 2009; 204: 237-45.
- [17] Beyer S, Dunkel V, Hasselmann U, Landgrebe R, Speckhardt H. Stress-corrosion in the liquid Zinc phase during high-temperature galvanization of HV screws of strength-10.0 with large dimensions. 2. Experimental-studies and theoretical-studies on damage mechanism and implications for practice. *Materialwiss Werkstofftech* 1994; 25: 459-70.
- [18] Bottcher HJ. Hot galvanization as a means of protection against corrosion in sea-water and in sea-atmosphere. *Metall*. 1968; 22: 1258-&.
- [19] Vollrath K. Hot galvanization for corrosion prevention. *Metall*. 2000; 54: 520-2.
- [20] Barbalat M, Lanarde L, Caron D, Meyer M, Vittonato J, Castillon F, et al. Electrochemical study of the corrosion rate of carbon steel in soil: Evolution with time and determination of residual corrosion rates under cathodic protection. *Corros Sci* 2012; 55: 246-53.
- [21] Diaz B, Swiatowska J, Maurice V, Pisarek M, Seyeux A, Zanna S, et al. Chromium and tantalum oxide nanocoatings prepared by filtered cathodic arc deposition for corrosion protection of carbon steel. *Surface & Coatings Technology*. 2012; 206: 3903-10.
- [22] Wang WH, Yi J, Chen L, Li XY. Numerical Simulation of Transient Process for Corrosion Environment in Coating Crevice with Cathodic Protection. *Journal of Computational and Theoretical Nanoscience*. 2012; 9: 1395-8.
- [23] Liu Y, Shi X. Cathodic protection technologies for reinforced concrete: introduction and recent developments. *Rev Chem Eng* 2009; 25: 339-88.
- [24] Liu Y, Shi X. Modeling cathodic prevention for unconventional concrete in salt-laden environment. *Anti-Corrosion Methods and Materials*. 2012; 59: 121-31.
- [25] Shi X, Fay L, Yang Z, Nguyen TA, Liu Y. Corrosion of deicers to metals in transportation infrastructure: introduction and recent developments. *Corros Rev* 2009; 27: 23-52.
- [26] Belkaid S, Tebbji K, Mansri A, Chetouani A, Hammouti B. Poly(4-vinylpyridine-hexadecyl bromide) as corrosion inhibitor for mild steel in acid chloride solution. *Res Chem Intermed* 2012; 38: 2309-25.
- [27] Guelsen A. Corrosion inhibition of mild steel by *Laurus nobilis* leaves extract as green inhibitor. *Res Chem Intermed* 2012; 38: 1311-21.
- [28] Javierre E, Garcia SJ, Mol JMC, Vermolen FJ, Vuik C, van der Zwaag S. Tailoring the release of encapsulated corrosion inhibitors from damaged coatings: Controlled release kinetics by overlapping diffusion fronts. *Prog Org Coat* 2012; 75: 20-7.
- [29] Singh A, Avyaya JN, Ebenso EE, Quraishi MA. Schiff's base derived from the pharmaceutical drug Dapsone (DS) as a new and effective corrosion inhibitor for mild steel in hydrochloric acid. *Res Chem Intermed* 2013; 39: 537-51.

- [30] Fink J. Petroleum Engineer's Guide to Oil Field Fluids: Gulf Professional Publishing; 2011.
- [31] Kuznetsov YI. Current state of the theory of metal corrosion inhibition. *Prot Met* 2002; 38: 103-11.
- [32] Agarwal P, Landolt D. Effect of anions on the efficiency of aromatic carboxylic acid corrosion inhibitors in near neutral media: Experimental investigation and theoretical modeling. *Corros Sci* 1998; 40: 673-91.
- [33] Ali SA, Al-Muallem HA, Rahman SU, Saeed MT. Bis-isoxazolidines: A new class of corrosion inhibitors of mild steel in acidic media. *Corros Sci* 2008; 50: 3070-7.
- [34] Alsabagh AM, Migahed MA, Awad HS. Reactivity of polyester aliphatic amine surfactants as corrosion inhibitors for carbon steel in formation water (deep well water). *Corros Sci* 2006; 48: 813-28.
- [35] Bentiss F, Lagrenée M, Traisnel M. 2,5-bis(n-pyridyl)-1,3,4-oxadiazoles as corrosion inhibitors for mild steel in acidic media. *Corrosion*. 2000; 56: 733-42.
- [36] de Souza FS, Spinelli A. Caffeic acid as a green corrosion inhibitor for mild steel. *Corros Sci* 2009; 51: 642-9.
- [37] Larabi L, Benali O, Mekelleche SM, Harek Y. 2-mercapto-1-methylimidazole as corrosion inhibitor for copper in hydrochloric acid. *Appl Surf Sci* 2006; 253: 1371-8.
- [38] Leng A, Stratmann M. THE INHIBITION OF THE ATMOSPHERIC CORROSION OF IRON BY VAPOR-PHASE-INHIBITORS. *Corros Sci* 1993; 34: 1657-&.
- [39] Moretti G, Quartarone G, Tassan A, Zingales A. Some derivatives of indole as mild steel corrosion inhibitors in 0.5 M sulphuric acid. *Br Corros J* 1996; 31: 49-54.
- [40] Muster TH, Hughes AE, Furman SA, Harvey T, Sherman N, Hardin S, et al. A rapid screening multi-electrode method for the evaluation of corrosion inhibitors. *Electrochim Acta* 2009; 54: 3402-11.
- [41] Zhang S, Tao Z, Li W, Hou B. The effect of some triazole derivatives as inhibitors for the corrosion of mild steel in 1 M hydrochloric acid. *Appl Surf Sci* 2009; 255: 6757-63.
- [42] Alvarez-Bustamante R, Negron-Silva G, Abreu-Quijano M, Herrera-Hernandez H, Romero-Romo M, Cuan A, et al. Electrochemical study of 2-mercaptoimidazole as a novel corrosion inhibitor for steels. *Electrochim Acta* 2009; 54: 5393-9.
- [43] Bazzi L, Kertit S, Hamdani M. SOME ORGANIC-COMPOUNDS AS INHIBITORS FOR THE CORROSION OF ALUMINUM-ALLOY-6063 IN DEAERATED CARBONATE SOLUTION. *Corrosion*. 1995; 51: 811-7.
- [44] Bahadur A. Development and evaluation of a low chromate corrosion inhibitor for cooling water systems. *Can Metall Q* 1998; 37: 459-68.
- [45] Taylor SR, Chambers BD. The discovery of non-chromate corrosion inhibitors for aerospace alloys using high-throughput screening methods. *Corros Rev* 2007; 25: 571-90.
- [46] Aramaki K. The healing effect of polymer films containing a non-chromate inhibitor on iron corrosion at scratched surfaces. *Corros Sci* 2000; 42: 1975-91.
- [47] Hurley BL, McCreery RL. Raman spectroscopy of monolayers formed from chromate corrosion inhibitor on copper surfaces. *J Electrochem Soc* 2003; 150: B367-B73.

- [48] Slobodyan ZV, Mahlatyuk LA, Nykyforchyn HM. Realization of synergism in 1-, 2-, 3-benzotriazole trimolybdate, tungstate, and chromate corrosion inhibitors. *Mater Sci* 2006; 42: 589-600.
- [49] Bastos AC, Ferreira MGS, Simoes AM. Comparative electrochemical studies of zinc chromate and zinc phosphate as corrosion inhibitors for zinc. *Prog Org Coat* 2005; 52: 339-50.
- [50] Darrin M. Chromate corrosion inhibitors in bimetallic systems - Compared by a scoring method based on visual observations. *Industrial and Engineering Chemistry-Analytical Edition*. 1941; 13: 0755-9.
- [51] Meziane M, Kermiche F, Fiaud C. Effect of molybdate ions as corrosion inhibitors of iron in neutral aqueous solutions. *Br Corros J* 1998; 33: 302-8.
- [52] Fujioka E, Nishihara H, Aramaki K. The inhibition of pit nucleation and growth on the passive surface of iron in a borate buffer solution containing Cl⁻ by oxidizing inhibitors. *Corros Sci* 1996; 38: 1915-33.
- [53] Alentejano CR, Aoki IV. Localized corrosion inhibition of 304 stainless steel in pure water by oxyanions tungstate and molybdate. *Electrochim Acta* 2004; 49: 2779-85.
- [54] Kendig M, Jeanjaquet S, Addison R, Waldrop J. Role of hexavalent chromium in the inhibition of corrosion of aluminum alloys. *Surface & Coatings Technology*. 2001; 140: 58-66.
- [55] Ravari FB, Mohammadi S, Dadgarinezhad A. Corrosion inhibition of mild steel in stimulated cooling water by blends of molybdate, nitrite and picrate as new anodic inhibitor. *Anti-Corrosion Methods and Materials*. 2012; 59: 182-9.
- [56] Mustafa CM, Dulal S. Molybdate and nitrite as corrosion inhibitors for copper-coupled steel in simulated cooling water. *Corrosion*. 1996; 52: 16-22.
- [57] Oung JC, Chiu SK, Shih HC. Mitigating steel corrosion in cooling water by molybdate based inhibitors. *Corrosion Prevention & Control*. 1998; 45: 156-62.
- [58] Li X, Deng S, Fu H. Sodium molybdate as a corrosion inhibitor for aluminium in H₃PO₄ solution. *Corros Sci* 2011; 53: 2748-53.
- [59] Mu GN, Li XH, Qu Q, Zhou J. Molybdate and tungstate as corrosion inhibitors for cold rolling steel in hydrochloric acid solution. *Corros Sci* 2006; 48: 445-59.
- [60] Moutarlier V, Gigandet MP, Pagetti J, Ricq L. Molybdate/sulfuric acid anodising of 2024-aluminium alloy: influence of inhibitor concentration on film growth and on corrosion resistance. *Surface & Coatings Technology*. 2003; 173: 87-95.
- [61] Robertson WD. Molybdate and Tungstate as corrosion inhibitors and the mechanism of inhibition. *J Electrochem Soc* 1951; 98: 94-100.
- [62] Chen JR, Chao HY, Lin YL, Yang IJ, Oung JC, Pan FM. Studies on carbon-steel corrosion in molybdate and silicate solutions as corrosion inhibitors. *Surf Sci* 1991; 247: 352-9.
- [63] Athey RD. Synthesis of S-substituted thioglycolates as corrosion inhibitors. *Corrosion*. 1977; 33: 147-.
- [64] Aramaki K. The inhibition effects of chromate-free, anion inhibitors on corrosion of zinc in aerated 0.5 M NaCl. *Corros Sci* 2001; 43: 591-604.
- [65] Gopi D, Govindaraju KM, Manimozhi S, Ramesh S, Rajeswari S. Inhibitors with biocidal functionalities to mitigate corrosion on mild steel in natural aqueous environment. *J Appl Electrochem* 2007; 37: 681-9.

- [66] Choi DJ, You SJ, Kim JG. Development of an environmentally safe corrosion, scale, and microorganism inhibitor for open recirculating cooling systems. *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing*. 2002; 335: 228-35.
- [67] Tsangaraki-Kaplanoglou I, Kanta A, Theohari S, Ninni V. Acid-dyes as corrosion inhibitors for mechanically pretreated aluminum. *Anti-Corrosion Methods and Materials*. 2010; 57: 6-12.
- [68] Liu XF, Huang SJ, Gu HC. Corrosion protection of an aluminum alloy with nontoxic compound inhibitors in chloride media. *Corrosion*. 2002; 58: 826-34.
- [69] Antonijevic MM, Petrovic MB. Copper corrosion inhibitors. A review. *Int J Electrochem Sci* 2008; 3: 1-28.
- [70] Leite AOS, Araujo WS, Margarit ICP, Correia AN, de Lima-Neto P. Evaluation of the anticorrosive properties of environmental friendly inorganic corrosion inhibitors pigments. *J Braz Chem Soc* 2005; 16: 756-62.
- [71] Balaskas AC, Kartsonakis IA, Snihirova D, Montemor MF, Kordas G. Improving the corrosion protection properties of organically modified silicate-epoxy coatings by incorporation of organic and inorganic inhibitors. *Prog Org Coat* 2011; 72: 653-62.
- [72] Amadeh A, Allahkaram SR, Hosseini SR, Moradi H, Abdolhosseini A. The use of rare earth cations as corrosion inhibitors for carbon steel in aerated NaCl solution. *Anti-Corrosion Methods and Materials*. 2008; 55: 135-43.
- [73] Forsyth M, Seter M, Hinton B, Deacon G, Junk P. New 'Green' Corrosion Inhibitors Based on Rare Earth Compounds. *Aust J Chem* 2011; 64: 812-9.
- [74] Fayala I, Dhouibi L, Novoa XR, Ben Ouezdou M. Effect of inhibitors on the corrosion of galvanized steel and on mortar properties. *Cement & Concrete Composites*. 2013; 35: 181-9.
- [75] Muster TH, Sullivan H, Lau D, Alexander DLJ, Sherman N, Garcia SJ, et al. A combinatorial matrix of rare earth chloride mixtures as corrosion inhibitors of AA2024-T3: Optimisation using potentiodynamic polarisation and EIS. *Electrochim Acta* 2012; 67: 95-103.
- [76] Forsyth M, Wilson K, Behrsing T, Forsyth C, Deacon GB, Phanasgoankar A. Effectiveness of rare-earth metal compounds as corrosion inhibitors for steel. *Corrosion*. 2002; 58: 953-60.
- [77] Davo B, de Damborenea JJ. Use of rare earth salts as electrochemical corrosion inhibitors for an Al-Li-Cu (8090) alloy in 3.56% NaCl. *Electrochim Acta* 2004; 49: 4957-65.
- [78] Aballe A, Bethencourt M, Botana FJ, Marcos M. CeCl₃ and LaCl₃ binary solutions as environment-friendly corrosion inhibitors of AA5083 Al-Mg alloy in NaCl solutions. *J Alloys Compd* 2001; 323: 855-8.
- [79] El-Meligi AA. Corrosion Preventive Strategies as a Crucial Need for Decreasing Environmental Pollution and Saving Economics. *Recent Patents on Corrosion Science*. 2010; 2: 22-33.
- [80] Jabeera B, Shibli SMA, Anirudhan TS. The synergistic inhibitive effect of tungstate with zinc ions on the corrosion of iron in aqueous environments. *Anti-Corrosion Methods and Materials*. 2002; 49: 408-16.
- [81] Bouayed M, Rabaa H, Srhiri A, Saillard JY, Ben Bachir A, Le Beuze A. Experimental and theoretical study of organic corrosion inhibitors on iron in acidic medium. *Corros Sci* 1999; 41: 501-17.
- [82] Amar H, Benzakour J, Derja A, Villemain D, Moreau B. A corrosion inhibition study of iron by phosphonic acids in sodium chloride solution. *J Electroanal Chem* 2003; 558: 131-9.

- [83] Angelica Hernandez-Alvarado L, Salvador Hernandez L, Maria Miranda J, Dominguez O. The protection of galvanised steel using a chromate-free organic inhibitor. *Anti-Corrosion Methods and Materials*. 2009; 56: 114-20.
- [84] Zin IM, Howard RL, Badger SJ, Scantlebury JD, Lyon SB. The mode of action of chromate inhibitor in epoxy primer on galvanized steel. *Prog Org Coat* 1998; 33: 203-10.
- [85] Kuznetsov YI, Rozenfeld IL, Agalarova TA. Protection of steel in sea-water by chromate inhibitors in conjunction with cathodic polarization. *Prot Met* 1982; 18: 438-41.
- [86] Brasher DM, Kingsbury AH. The study of the passivity of metals in inhibitor solutions, using radioactive tracers. 1. the action of neutral chromates on iron and steel. *Trans Faraday Soc* 1958; 54: 1214-22.
- [87] Brasher DM, Mercer AD. Radiotracer studies of passivity of metals in inhibitor solutions. 3. influence of pH and oxygen content of chromate solutions on film growth on mild steel. *Trans Faraday Soc* 1965; 61: 803-&.
- [88] Romagnoli R, Vetere VF. Heterogeneous reaction between steel and Zinc phosphate. *Corrosion*. 1995; 51: 116-23.
- [89] Ju H, Li Y. Nicotinic acid as a nontoxic corrosion inhibitor for hot dipped Zn and Zn-Al alloy coatings on steels in diluted hydrochloric acid. *Corros Sci* 2007; 49: 4185-201.
- [90] Al-Rawajfeh AE, Al-Shamaileh EM. Inhibition of corrosion in steel water pipes by ammonium pyrrolidine dithiocarbamate (APDTC). *Desalination*. 2007; 206: 169-78.
- [91] Morad MS. Effect of amino acids containing sulfur on the corrosion of mild steel in phosphoric acid solutions containing Cl⁻, F⁻ and Fe³⁺ ions: Behavior under polarization conditions. *J Appl Electrochem* 2005; 35: 889-95.
- [92] Okafor PC, Ebenso EE. Inhibitive action of Carica papaya extracts on the corrosion of mild steel in acidic media and their adsorption characteristics. *Pigment & Resin Technology*. 2007; 36: 134-40.
- [93] Kahraman R. Inhibition of atmospheric corrosion of mild steel by sodium benzoate treatment. *J Mater Eng Perform* 2002; 11: 46-50.
- [94] Al-Mathami A, Saricimen H, Kahraman R, Al-Zahrani M, Al-Dulaijan S. Inhibition of atmospheric corrosion of mild steel by sodium dihydrogen orthophosphate treatment. *Anti-Corrosion Methods and Materials*. 2004; 51: 121-9.
- [95] Saricimen H. Corrosion of inhibitor treated carbon steel during wet/dry cycling tests. *Anti-Corrosion Methods and Materials*. 2009; 56: 162-7.
- [96] Rajendran S, Apparao BV, Palaniswamy N. Corrosion inhibition by phosphonic acid -Zn²⁺ systems for mild steel in chloride medium. *Anti-Corrosion Methods and Materials*. 2000; 47: 359-65.
- [97] Rajendran S, Apparao BV, Palaniswamy N. Synergistic effect of ethyl phosphonate and Zn²⁺ in low chloride media. *Anti-Corrosion Methods and Materials*. 1998; 45: 338-+.
- [98] Rajendran S, Apparao BV, Mani A, Palaniswamy N. Corrosion inhibition by ATMP-molybdate-Zn²⁺ system in low chloride media. *Anti-Corrosion Methods and Materials*. 1998; 45: 25-+.
- [99] Rajendran S, Apparao BV, Palaniswamy N. Synergistic, antagonistic and biocidal effects of amino (trimethylene phosphonic acid), polyacrylamide and Zn²⁺ on the inhibition of corrosion of mild steel in neutral aqueous environment. *Anti-Corrosion Methods and Materials*. 1997; 44: 308-13.

- [100] Narmada P, Rao MV, Venkatachari G, Rao BVA. Synergistic inhibition of carbon steel by tertiary butyl phosphonate, zinc ions and citrate. *Anti-Corrosion Methods and Materials*. 2006; 53: 310-4.
- [101] Rajendran S, Apparao BV, Palaniswamy N. Mechanism of inhibition of corrosion of mild steel by polyacrylamide, phenyl phosphonate and Zn^{2+} . *Anti-Corrosion Methods and Materials*. 1999; 46: 111-6.
- [102] Rajendran S, Apparao BV, Palaniswamy N. Corrosion inhibition by phenylphosphonate and Zn^{2+} . *Anti-Corrosion Methods and Materials*. 1998; 45: 158-+.
- [103] Rajendran S, Apparao BV, Palaniswamy N. HEDP- Zn^{2+} : a potential inhibitor system for mild steel in low chloride media. *Anti-Corrosion Methods and Materials*. 2000; 47: 83-7.
- [104] Abdallah M, El-Etre AY, Soliman MG, Mabrouk EM. Some organic and inorganic compounds as inhibitors for carbon steel corrosion in 3.5 percent NaCl solution. *Anti-Corrosion Methods and Materials*. 2006; 53: 118-23.
- [105] Boucherit MN, Amzert S-A, Arbaoui F, Hanini S, Hammache A. Pitting corrosion in presence of inhibitors and oxidants. *Anti-Corrosion Methods and Materials*. 2008; 55: 115-22.
- [106] Shibli SMA, Kumary VA. Inhibitive effect of calcium gluconate and sodium molybdate on carbon steel. *Anti-Corrosion Methods and Materials*. 2004; 51: 277-81.
- [107] Malik H. Corrosion inhibition by N coco-amine-2-propionic acid on mild steel in CO_2 saturated 5 per cent NaCl at pH 6.5. *Anti-Corrosion Methods and Materials*. 1999; 46: 434-8.
- [108] Malik H. Charge and pH effects on inhibitor performance. *Anti-Corrosion Methods and Materials*. 2001; 48: 364-70.
- [109] Sahin M, Bilgic S, Yilmaz H. The inhibition effects of some cyclic nitrogen compounds on the corrosion of the steel in NaCl mediums. *Appl Surf Sci* 2002; 195: 1-7.
- [110] Ochoa N, Baril G, Moran F, Pebere N. Study of the properties of a multi-component inhibitor used for water treatment in cooling circuits. *J Appl Electrochem* 2002; 32: 497-504.
- [111] Ashour EA, Hegazy HS. Inhibitive effect of benzotriazole on the stress corrosion cracking of type 316 stainless steel in chloride and thiosulfate containing solutions. *Anti-Corrosion Methods and Materials*. 2003; 50: 291-5.
- [112] Wei ZQ, Duby P, Somasundaran P. Pitting inhibition of stainless steel by surfactants: an electrochemical and surface chemical approach. *J Colloid Interface Sci* 2003; 259: 97-102.
- [113] Abd El-Ghaffar MA, Youssef EAM, Darwish WM, Helaly FM. A novel series of corrosion inhibitive polymers for steel protection. *J Elastomers Plast* 1998; 30: 68-94.
- [114] Mahjani MG, Sabzali M, Jafarian M, Neshati J. An investigation of the effects of inorganic inhibitors on the corrosion rate of aluminum alloy using electrochemical noise measurements and electrochemical impedance spectroscopy. *Anti-Corrosion Methods and Materials*. 2008; 55: 208-16.
- [115] Onal AN, Aksut AA. Corrosion inhibition of aluminium alloys by tolyltriazole in chloride solutions. *Anti-Corrosion Methods and Materials*. 2000; 47: 339-48.
- [116] Sherif E-SM. Corrosion and Corrosion Inhibition of Aluminum in Arabian Gulf Seawater and Sodium Chloride Solutions by 3-Amino-5-Mercapto-1,2,4-Triazole. *Int J Electrochem Sci* 2011; 6: 1479-92.
- [117] Allachi H, Chaouket F, Draoui K. Protection against corrosion in marine environments of AA6060 aluminium alloy by cerium chlorides. *J Alloys Compd* 2010; 491: 223-9.

- [118] Lamaka SV, Zheludkevich ML, Yasakau KA, Montemor MF, Ferreira MGS. High effective organic corrosion inhibitors for 2024 aluminium alloy. *Electrochim Acta* 2007; 52: 7231-47.
- [119] Bereket G, Yurt A. The inhibition effect of amino acids and hydroxy carboxylic acids on pitting corrosion of aluminum alloy 7075. *Corros Sci* 2001; 43: 1179-95.
- [120] Quinet M, Neveu B, Moutarlier V, Audebert P, Ricq L. Corrosion protection of sol-gel coatings doped with an organic corrosion inhibitor: Chloranil. *Prog Org Coat* 2007; 58: 46-53.
- [121] Elliot J, Cook R. Nanoparticle-Based Corrosion Inhibitors for Aerospace Aluminum. *Tri-Service Corrosion Conference* 2007.
- [122] Sharman S. Evaluation & Performance of Chemical Surface Treatments for Maintenance. *NACE International Corrosion Conference and Expo Paper 090062009*. p. 1-17.
- [123] Collazo A, Novoa XR, Perez C, Puga B. EIS study of the rust converter effectiveness under different conditions. *Electrochim Acta* 2008; 53: 7565-74.
- [124] Collazo A, Novoa XR, Perez C, Puga B. The corrosion protection mechanism of rust converters: An electrochemical impedance spectroscopy study. *Electrochim Acta* 2010; 55: 6156-62.
- [125] Barrero CA, Ocampo LM, Arroyave CE. Possible improvements in the action of some rust converters. *Corros Sci* 2001; 43: 1003-18.
- [126] Bolivar F, Barrero CA, Minotas J, Morales AL, Greneche JM. Variable temperature Mossbauer study of some rust converters. *Hyperfine Interact* 2003; 148: 219-25.
- [127] Caseres L. Evaluation of Zn-rich Primers and Rust Converters for Corrosion Protection of Steel. *US Army Corrosion Summit Clearwater Beach. FL* 2009. p. 1-22.
- [128] Liu ZY, Li XG, Cheng YF. Electrochemical state conversion model for occurrence of pitting corrosion on a cathodically polarized carbon steel in a near-neutral pH solution. *Electrochim Acta* 2011; 56: 4167-75.
- [129] Maier B, Frankel GS. Pitting Corrosion of Silica-Coated Type 304 Stainless Steel Under Thin Electrolyte Layers. *Corrosion*. 2011; 67.
- [130] Caceres L, Vargas T, Herrera L. Influence of pitting and iron oxide formation during corrosion of carbon steel in unbuffered NaCl solutions. *Corros Sci* 2009; 51: 971-8.
- [131] Hastuty S, Nishikata A, Tsuru T. Pitting corrosion of Type 430 stainless steel under chloride solution droplet. *Corros Sci* 2010; 52: 2035-43.
- [132] Bentiss F, Traisnel M, Gengembre L, Lagrenée M. A new triazole derivative as inhibitor of the acid corrosion of mild steel: electrochemical studies, weight loss determination, SEM and XPS. *Appl Surf Sci* 1999; 152: 237-49.
- [133] Finsgar M, Fassbender S, Hirth S, Milosev I. Electrochemical and XPS study of polyethyleneimines of different molecular sizes as corrosion inhibitors for AISI 430 stainless steel in near-neutral chloride media. *Mater Chem Phys* 2009; 116: 198-206.
- [134] Gasparac R, Martin CR, Stupnisek-Lisac E, Mandic Z. In situ and ex situ studies of imidazole and its derivatives as copper corrosion inhibitors II. AC impedance, XPS, and SIMS studies. *J Electrochem Soc* 2000; 147: 991-8.
- [135] Lopez DA, Schreiner WH, de Sanchez SR, Simison SN. The influence of inhibitors molecular structure and steel microstructure on corrosion layers in CO₂ corrosion - An XPS and SEM characterization. *Appl Surf Sci* 2004; 236: 77-97.

- [136] Olivares-Xometl O, Likhanova NV, Martinez-Palou R, Dominguez-Aguilar MA. Electrochemistry and XPS study of an imidazoline as corrosion inhibitor of mild steel in an acidic environment. *Materials and Corrosion-Werkstoffe Und Korrosion*. 2009; 60: 14-21.
- [137] Bairamow AK, Zakipour S, Leygraf C. AN XPS INVESTIGATION OF DICHROMATE AND MOLYBDATE INHIBITORS ON ALUMINUM. *Corros Sci* 1985; 25: 69-73.
- [138] Swift A, Paul AJ, Vickerman JC. INVESTIGATION OF THE SURFACE-ACTIVITY OF CORROSION-INHIBITORS BY XPS AND TIME-OF-FLIGHT SIMS. *Surf Interface Anal* 1993; 20: 27-35.
- [139] Finsgar M, Kovac J, Milosev I. Surface Analysis of 1-Hydroxybenzotriazole and Benzotriazole Adsorbed on Cu by X-Ray Photoelectron Spectroscopy. *J Electrochem Soc* 2010; 157: C52-C60.
- [140] Finsgar M, Peljhan S, Kokalj A, Kovac J, Milosev I. Determination of the Cu₂O Thickness on BTAH-Inhibited Copper by Reconstruction of Auger Electron Spectra. *J Electrochem Soc* 2010; 157: C295-C301.
- [141] Lister TE, Pinhero PJ. The effect of localized electric fields on the detection of dissolved sulfur species from Type 304 stainless steel using scanning electrochemical microscopy. *Electrochim Acta* 2003; 48: 2371-8.
- [142] Gonzalez-Garcia Y, Burstein GT, Gonzalez S, Souto RM. Imaging metastable pits on austenitic stainless steel in situ at the open-circuit corrosion potential. *Electrochem Commun* 2004; 6: 637-42.
- [143] Eckhard K, Etienne M, Schulte A, Schuhmann W. Constant-distance mode AC-SECM for the visualisation of corrosion pits. *Electrochem Commun* 2007; 9: 1793-7.
- [144] Davoodi A, Pan J, Leygraf C, Norgren S. Integrated AFM and SECM for in situ studies of localized corrosion of Al alloys. *Electrochim Acta* 2007; 52: 7697-705.
- [145] Bastos AC, Simoes AM, Gonzalez S, Gonzalez-Garcia Y, Souto RM. Application of the scanning electrochemical microscope to the examination of organic coatings on metallic substrates. *Prog Org Coat* 2005; 53: 177-82.
- [146] Bastos AC, Simoes AM, Gonzalez S, Gonzalez-Garcia Y, Souto RM. Imaging concentration profiles of redox-active species in open-circuit corrosion processes with the scanning electrochemical microscope. *Electrochem Commun* 2004; 6: 1212-5.
- [147] Seegmiller JC, Buttry DA. A SECM study of heterogeneous redox activity at AA2024 surfaces. *J Electrochem Soc* 2003; 150: B413-B8.
- [148] Malik MA, Kulesza PJ. Monitoring of conductivity changes in passive layers by scanning electrochemical microscopy in feedback mode: Localization of pitting precursor sites on surfaces of multimetallic phase materials. *Anal Chem* 2007; 79: 3996-4005.
- [149] Mansikkamaki K, Haapanen U, Johans C, Kontturi K, Valden M. Adsorption of benzotriazole on the surface of copper alloys studied by SECM and XPS. *J Electrochem Soc* 2006; 153: B311-B8.
- [150] Izquierdo J, Nagy L, Santana JJ, Nagy G, Souto RM. A novel microelectrochemical strategy for the study of corrosion inhibitors employing the scanning vibrating electrode technique and dual potentiometric/amperometric operation in scanning electrochemical microscopy: Application to the study of the cathodic inhibition by benzotriazole of the galvanic corrosion of copper coupled to iron. *Electrochim Acta* 2011; 58: 707-16.

- [151] Fan H, Li S, Zhao Z, Wang H, Shi Z, Zhang L. Inhibition of brass corrosion in sodium chloride solutions by self-assembled silane films. *Corros Sci* 2011; 53: 4273-81.
- [152] Izquierdo J, Jose Santana J, Gonzalez S, Souto RM. Uses of scanning electrochemical microscopy for the characterization of thin inhibitor films on reactive metals The protection of copper surfaces by benzotriazole. *Electrochim Acta* 2010; 55: 8791-800.
- [153] Souto RM, Santana JJ, Fernandez-Merida L, Gonzalez S. Sensing electrochemical activity in polymer coated metals during the early stages of coating degradation-Effect of the polarization of the substrate. *Electrochim Acta* 2011; 56: 9596-601.
- [154] Lu L, Li X, Gao F. Localized Electrochemical Study on the Interface Corrosion Between Organic Coating/Metal Substrate. *Progress in Chemistry*. 2011; 23: 1618-26.
- [155] Izquierdo J, Nagy L, Varga A, Bitter I, Nagy G, Souto RM. Scanning electrochemical microscopy for the investigation of corrosion processes: Measurement of Zn^{2+} spatial distribution with ion selective microelectrodes. *Electrochim Acta* 2012; 59: 398-403.
- [156] Arutunow A, Darowicki K, Zielinski A. Atomic force microscopy based approach to local impedance measurements of grain interiors and grain boundaries of sensitized AISI 304 stainless steel. *Electrochim Acta* 2011; 56: 2372-7.
- [157] Aubert I, Saintier N, Olive JM. Crystal plasticity computation and atomic force microscopy analysis of the internal hydrogen-induced slip localization on polycrystalline stainless steel. *Scr Mater* 2012; 66: 698-701.
- [158] Nagarajan S, Rajendran N. Crevice corrosion behaviour of superaustenitic stainless steels: Dynamic electrochemical impedance spectroscopy and atomic force microscopy studies. *Corros Sci* 2009; 51: 217-24.
- [159] Souier T, Martin F, Bataillon C, Cousty J. Local electrical characteristics of passive films formed on stainless steel surfaces by current sensing atomic force microscopy. *Appl Surf Sci* 2010; 256: 2434-9.
- [160] John D, Blom A, Bailey S, Nelson A, Schulz J, De Marco R, et al. The application of neutron reflectometry and atomic force microscopy in the study of corrosion inhibitor films. *Physica B-Condensed Matter*. 2006; 385-86: 924-6.
- [161] Cho SH, Kang CG, Lee SM. Development of evaluation technique for microcharacteristics of thixoforged wrought aluminum alloy by nanoindentation and atomic force microscopy. *Int J Adv Manuf Technol* 2009; 42: 892-909.
- [162] Hahm J, Sibener SJ. Stress-modified electrochemical reactivity of metallic surfaces: atomic force microscopy imaging studies of nickel and alloyed aluminum. *Appl Surf Sci* 2000; 161: 375-84.
- [163] Iannuzzi M, Frankel GS. Inhibition of Aluminum Alloy 2024 Corrosion by Vanadates: An In Situ Atomic Force Microscopy Scratching Investigation. *Corrosion*. 2007; 63: 672-88.
- [164] Kim HH, Kang CG. Evaluation of Precipitation Hardening Characteristics of Rheology-Forged Al 7075 Aluminum Alloy Using Nano- or Microindentation and Atomic Force Microscopy. *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*. 2010; 41A: 696-705.
- [165] Simpson TRE, Watts JF, Zhdan PA, Castle JE, Digby RP. A combined atomic force microscopy (AFM)/X-ray photoelectron spectroscopy (XPS) study of organosilane molecules adsorbed on the aluminium alloy L157-T6. *J Mater Chem* 1999; 9: 2935-41.

- [166] Fang TH, Wang TH, Wu KT. Local oxidation of titanium films by non-contact atomic force microscopy. *Microelectron Eng* 2008; 85: 1616-23.
- [167] Karagkiozaki V, Logothetidis S, Kalfagiannis N, Lousinian S, Giannoglou G. Atomic force microscopy probing platelet activation behavior on titanium nitride nanocoatings for biomedical applications. *Nanomedicine-Nanotechnology Biology and Medicine*. 2009; 5: 64-72.
- [168] Vasu K, Krishna MG, Padmanabhan KA. Conductive-atomic force microscopy study of local electron transport in nanostructured titanium nitride thin films. *Thin Solid Films* 2011; 519: 7702-6.
- [169] Vyas V, Podesta A, Milani P. Probing Nanoscale Interactions on Biocompatible Cluster-Assembled Titanium Oxide Surfaces by Atomic Force Microscopy. *J Nanosci Nanotechnol* 2011; 11: 4739-48.
- [170] Bucko M, Rogan J, Stevanovic SI, Peric-Grujic A, Bajat JB. Initial corrosion protection of Zn-Mn alloys electrodeposited from alkaline solution. *Corros Sci* 2011; 53: 2861-71.
- [171] Cimat KA, Mahurin SM, Meyer KA, Shaw RW. Nanoscale Chemical Imaging of Zinc Oxide Nanowire Corrosion. *J Phys Chem C* 2012; 116: 10405-14.
- [172] Gnanamuthu RM, Mohan S, Saravanan G, Lee CW. Comparative study on structure, corrosion and hardness of Zn-Ni alloy deposition on AISI 347 steel aircraft material. *J Alloys Compd* 2012; 513: 449-54.
- [173] Topuz O, Aydin C, Uzun O, Inan U, Alacam T, Tunca YM. Structural effects of sodium hypochlorite solution on RaCe rotary nickel-titanium instruments: an atomic force microscopy study. *Oral Surgery Oral Medicine Oral Pathology Oral Radiology and Endodontology*. 2008; 105: 661-5.

Chapter 6. Test Methods and Online Monitoring Techniques for Anti-Corrosion Practices

The previous chapters discussed how inhibitors and coatings can be used to reduce the rate of corrosion. However, theories are always one door away from reality, and the key to open it is experimental analysis. In this chapter, we will discuss some specific testing methods and online monitoring systems to turn our theories from last chapters into real applications.

There are two main topics in this chapter, first various test methods are examined and then some online monitoring techniques that provide valuable real time corrosion information are presented.

1. Test Methods

In general, chloride solutions are one of the most corrosive. In order to prevent corrosion from its extreme character, a variety of test methods to assess chloride corrosion to metals are developed. Each method provides significant results depending on the application. Among these test methods are laboratory test methods, on site test methods and online monitoring systems. In order to predict and manage corrosion damage, the original condition with respect to corrosion must be defined and the corrosivity of the environment and the exposure time need to be measured. Accurate corrosion projections are difficult to obtain due to the nature and time involved with corrosion. While accelerated laboratory techniques are constantly changing in order to acquire accurate results that can be applied to real time situations, outdoor exposure testing is very time consuming (**Kinzie, 2003**).

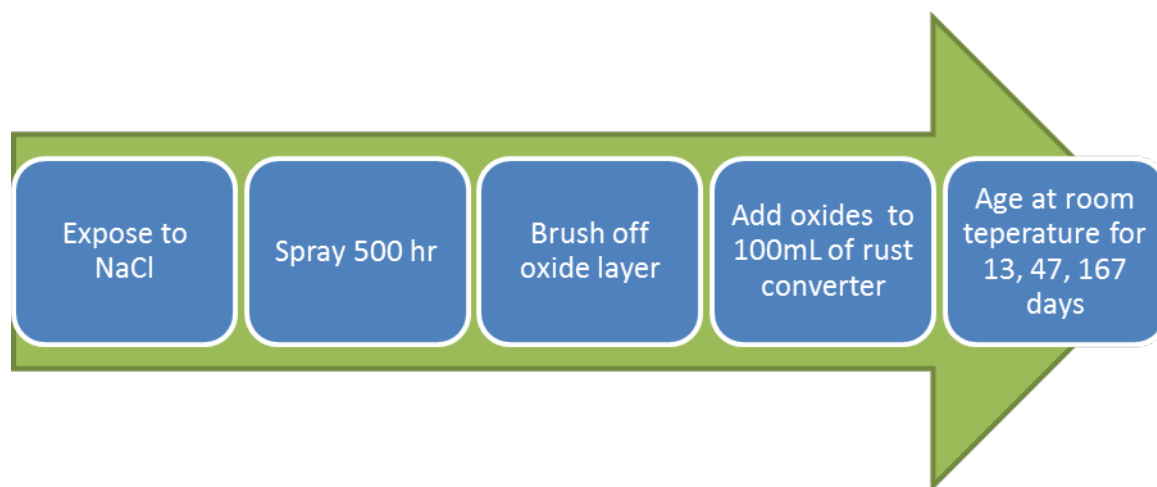


Figure 1. Mild Steel corrosion test.

Recently, a survey performed by Steel Structures Painting Council (SSPC) determined that the salt spray test is the most widely used corrosion assessment method (**Granata, 2005**).

Recently, salt spray test had been found as the most widely corrosion assessment method by Steel Structures Painting Council (SSPC). When mild steel plates of size (150mm x 100mm x 2mm) were corroded in a salt spray chamber, it follows the steps below:

The samples were then dried and then underwent electrochemical testing. The electrochemical testing consisted of electrochemical impedance spectroscopy (EIS) (**Collazo, 2010a**).

The following test method was used by Schmidt to test coatings (**Schmidt, 2006a**). All tested

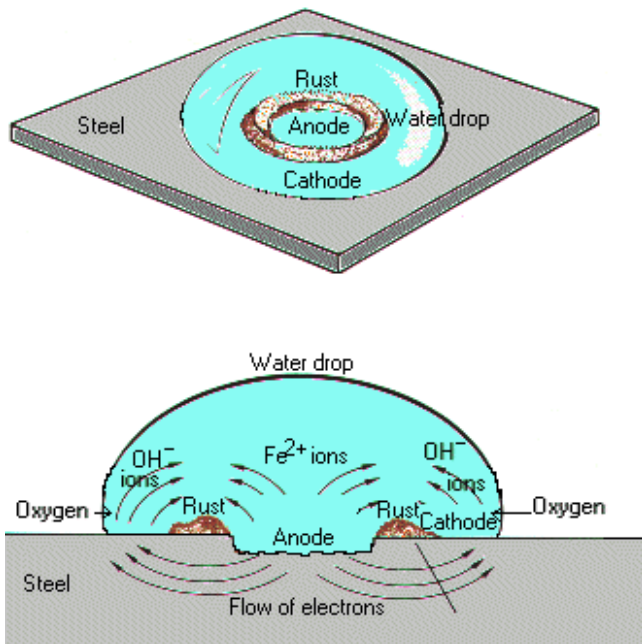


Figure 2. Electrochemical reaction.

In another test Schmidt used ASTM standard B117 Salt Spray (Fog) Test, SAE J2334 test and atmospheric exposure. ASTM standard B117 Salt Spray (Fog) Test involves a controlled laboratory exposure designed to accelerate results versus long-term outdoor exposure testing. In the B117 method a salt solution is sprayed as a mist on specimens in a constant temperature chamber. This test is considered to be an inaccurate representation of the corrosion mechanism due to the fact that the salt spray is continuously applied, which allows for no drying period. This drying period, which allows for the formation of protective layers, is critical in corrosion prevention. Compare to ASTM B117 test, an accelerated corrosion test method created by the Society of Automotive Engineers (SAE), SAE J2334, exposes metal specimens to changing climates over time in an enclosed chamber. The SAE J2334 test, uses a salt solution mixture of 0.5% NaCl, 0.1% CaCl_2 and 0.075% NaHCO_3 and consists of three stages: the humid stage with 6 hours of exposure at 50°C and 100% humidity, the salt application stage with a duration of 15 minutes at ambient conditions, and the dry stage with an exposure of 17 hours and 45 minutes at 60°C and 50% relative humidity. This test has been considered as an alternative for ASTM B117 because it allows dry stage and has various corrosive ions in its spray solution. It also has been found that 80 cycles of SAE J2334 test corresponds to 5 years of on-vehicle testing which reduced the expense of outdoor testing.

coatings were applied to 10.2 cm x 15.2 cm x 0.32 cm ANSI 1018 flat steel panels. A scribe of 6.6 cm by 0.32 cm was marked into each of the samples at a depth of 0.064 cm and 0.015 cm on the continuous hot-dip samples. The samples were exposed on racks at an angle of 30° from horizontal, 25 m from the ocean and exposed to atmospheric conditions. Temperature, relative humidity, dew point, solar energy, wind speed and direction, time of wetness, rainfall, and chloride concentration were all recorded daily. These were exposed for 20 months. There were 2 replicates of each coating tested and they were analyzed 6 times. Tested pictures were taken, the samples were physically observed, and electrochemical tests were performed.



Figure 3. ASTM B117 test chamber and various specimens as loaded into the salt spray.

Atmospheric exposure is another issue in corrosion study. It involves specimens at 30° angle from the horizontal exposed on racks to the ocean-front atmosphere.

An exposure of 24 months period study found when temperature, relative humidity, dew point, solar energy, wind speed and direction, time of wetness, rainfall, and chloride concentration recorded daily, (detailed analyses of the specimens were performed six times throughout the exposure period), the results from various types of tests don't correlate well with one another but the comparing of the coating systems to one another within each type of test is effective (Schmidt, 2005a).

A study had tested the difference between ISO 20430 and ASTM D5894 methods with three two coat systems. **Table 1.** below is the detailed information of those systems.

Table 1. Two coat systems

System No.	Primer	Finish	Description	Dry Film Thickness Applied
1	Zinc Phosphate Epoxy	Zinc Phosphate Epoxy	A two Component, Low VOC, high solids, fast curing epoxy primer/finish containing zinc phosphate. Used for primer and finish	2 coats @ 7.9 mils (200 microns)
2	Surface Tolerant Epoxy	Surface Tolerant Epoxy	A low VOC, two component high build, high solids, surface tolerant epoxy maintenance coating. Used for primer and finish.	2 coats @ 7.9 mils (200 microns)
3	Modified Epoxy	Modified Epoxy	A two component, low VOC, high solids, modified epoxy barrier coat. Used for primer and finish	2 coats @ 7.9 mils (200 microns)

ISO 20430 test method is a cyclic corrosion test used to evaluate a coating system performance for use in a marine environment classified as C5-M as per ISO 12944, Part 2 (shown in Figure 4).

The ASTM D5894 is another cyclic corrosion test specific to industrial onshore environments. The coating test panels are exposed to UV-A for one week with 4 hours dry UV-A at 60°C and 4 hours condensation at 50°C as per ASTM G53 and prohesion salt spray (0.35% (NH₄)₂SO₄ and 0.05%NaCl) for one week with one hour spray at 25°C and one hour dry time at 35°C as per ASTM G85. The test panels were scribed with a horizontal cut into the coating system. In the immersion test method ISO 2812-2:2007, coated test panels are immersed in water. The panels are positioned such that 75% of the panel is immersed (shown in **Figure 5. Sharman, 2009a**).

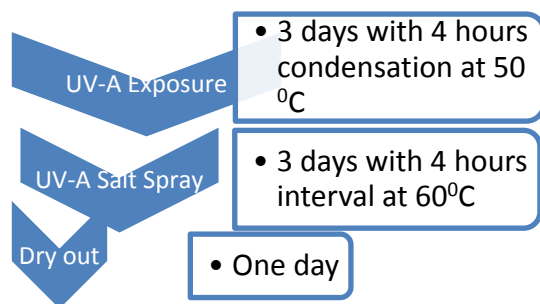


Figure 4. ISO 20430 test procedure.

As seen from the corrosion creep data, even in similar cyclic corrosion tests, the variability of data is obvious. It has proven the importance of performing various tests for the purpose of accuracy of data and avoiding failure of product in real life.

The PNS/NACE test is another common method for investigating corrosion effects. It is a modification of the National Association of Corrosion Engineers (NACE) Standard TM0169-95 by the Pacific Northwest Snowfighters (PNS). This test method consists of applying 30 ml of a 3% chemical deicer solution per square inch to the surface of a coupon for testing. A cyclic immersion procedure is used with 10 minutes exposure in the solution then 50 minutes air exposure. This gravimetric method of multiple parallel coupons is continued for 72 hours. The results from the gravimetric method are expressed as the average corrosion rate over a period of time. A percent corrosion rate (PCR) relating to the solution corrosivity is calculated from the weight loss. Electrochemical techniques are suggested as an alternative to gravimetric methods since corrosion mechanisms and kinetics data can be obtained in a timely manner (Pacific Northwest Snowfighters, 2004).

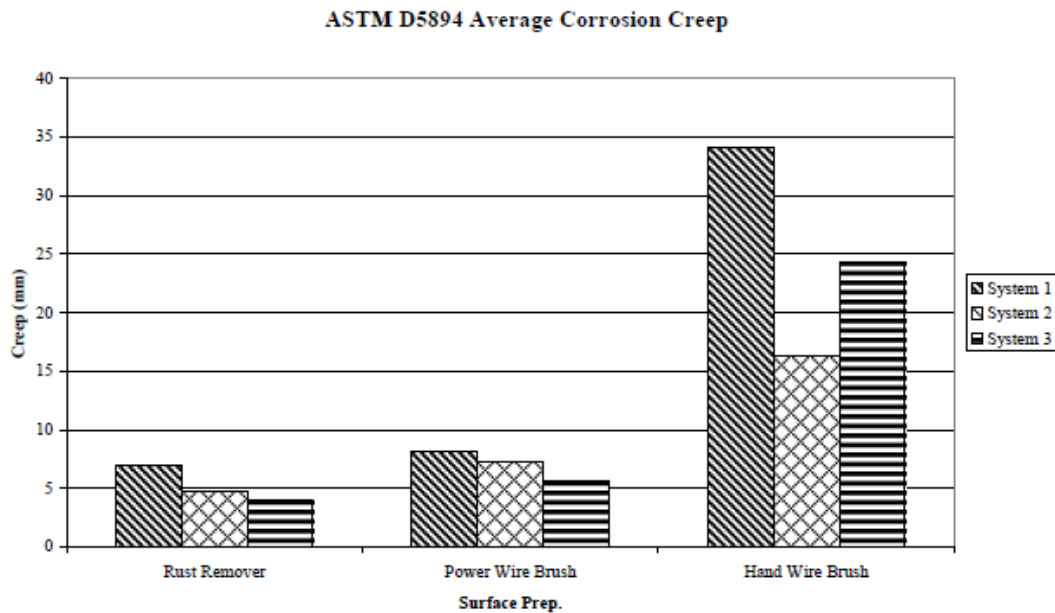


Figure 5. Average corrosion creep after ISO 20340 and ASTM D5894 exposure.

A little different test approach is the SHRP H-205.7 test method developed by the Strategic Highway Research Program (SHRP) to analyze the effectiveness of corrosion inhibiting additive in deicing substances. This test method uses continuous immersion to evaluate the corrosive effects of deicers on metal. This test does not have a wet-dry cycle which is an inaccurate representation of field exposures. A long exposure time is required before weight loss data is collected (**Chappelow et al., 1992**).

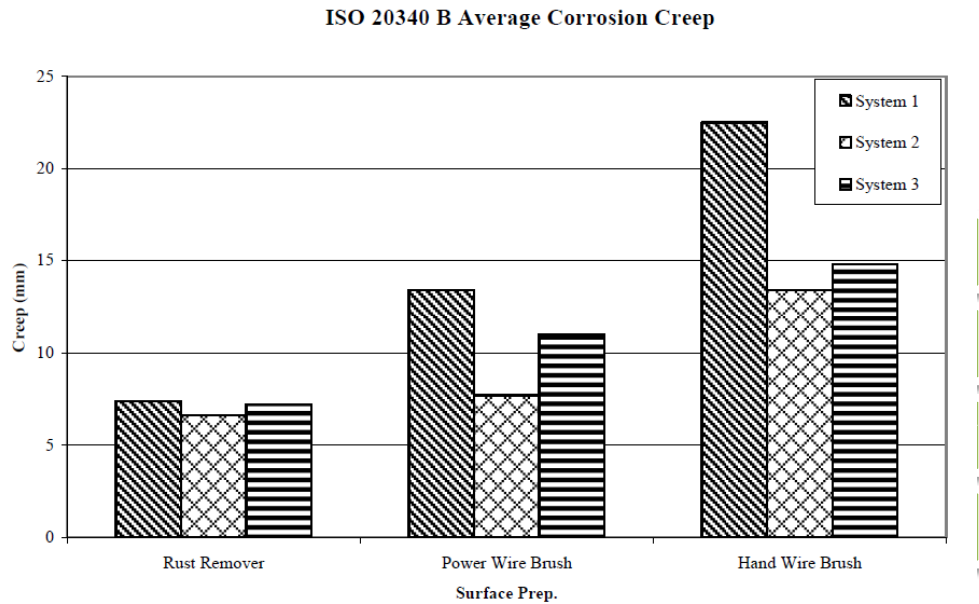


Figure 6. Durability test event.

Compared to civilian objects, the US Army has always been affected by corrosion and its negative effects. Consequently, the US Army has developed an accelerated corrosion and durability test to collect corrosion and material performance data that can be related to service life of military vehicles in highly corrosive environments. This accelerated corrosion testing is based on tests developed by General Motors (GM). It has been found that the test has been able to simulate 10 years of cosmetic corrosion but only 3 years of crevice corrosion. It combines accelerated corrosion test and durability test which introduce typical input stresses increasing the natural corrosion rates. The durability test events introduce typical situations encountered over the service life of the vehicle (see Figure 6). The application portion of the test includes a grit trough, salt mist, and humidity chamber. The grit trough allows small particles to accumulate on surfaces which increases time of wetness and provides abrasive particles to the coatings, the salt mist applies a high concentration salt solution to the vehicle typical of roadways that contain deicing salts and the use of the high temperature and high humidity chamber is to increase the rate of corrosion (**Ault, 1999**).

While most corrosion tests show their high efficiency of saving costs on corrosion effect, researchers have experienced that the downside of those experiments is the long time period. For example, salt spray accelerated test methods requires 2000 hours of exposure and electrochemical measurements can take up to 10 weeks for results. Accelerated test methods like this have been proven to be very difficult to develop when time of failure needs to decrease while failure mechanism remains the same. Some discoveries show that corrosion resistant performance can be obtained through thermal cycling and monitoring low frequency impedance changes of coating systems. Dr. Bierwagen, a research professor from North Dakota State University, discovered that the use of thermal cycling paired with electrochemical impedance spectroscopy provides a faster, quantitative method to evaluate coating corrosion resistance, which leads to corrosion resistance results obtained within a week of testing (**Bierwagen, et. al. 2000**).

Recently, a new system called the wire beam electrode (WBE) uses a multi electrode technique which can be applied to corrosion studies. An electrochemically non-uniform metal surface occurs when a metal surface is exposed to an electrolyte causing localized defects in protective coatings and a polarization voltage across the surface. Galvanic corrosion current and corrosion

potential are measured and used to assess the distribution of corrosion rates with the wire beam electrode system (Tan, 1999).

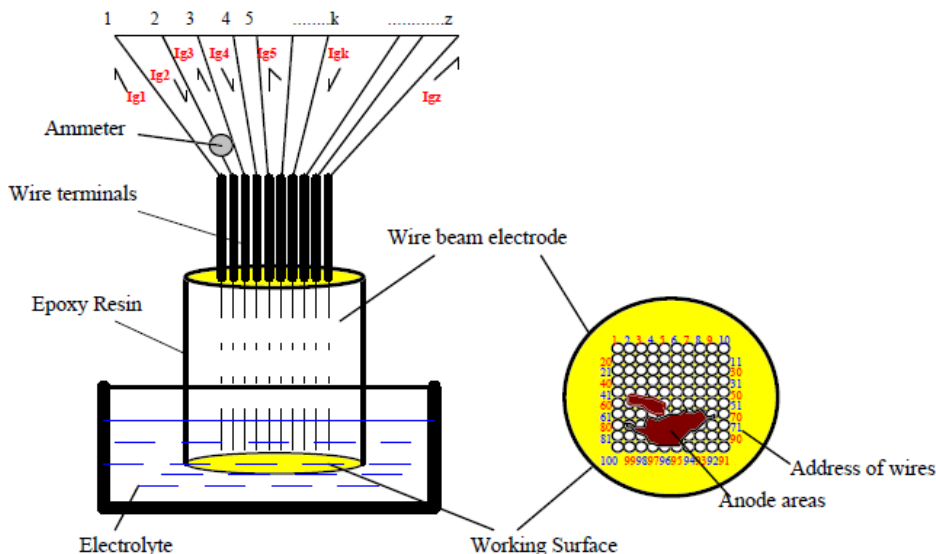


Figure 7. The conceptual design of a WBE system.

Crevice corrosion has been studied using traditional methods involving weight loss measurements and inspection which provide details of mechanisms and processes. However, the wire beam electrode system is able to assess instantaneous corrosion rates. (Tan et al., 2001b) Electrochemical noise resistance coupled with wire beam electrode methods has offered advantages for determining corrosion rate and patterns. The noise resistance is defined as the ratio of the standard deviations of potential noise and of the current measured noise. The noise resistance has been found to be equivalent to the polarization resistance therefore being used to determine rates of corrosion (Tan, 2003). It was determined that the time-average noise resistances from stainless steel sensors provided a good relationship with solution corrosivity. Furthermore, coupled multielectrode array sensors also provided a good correlation with solution corrosivity (Yang et al., 2004).

With advancements in material science, engineering, and testing methods, many improvements have been made to corrosion protective systems in the past decades. However, developing accurate accelerated test methods remains a major challenge. It has been found that correlations between coating performance and electrical properties offer valuable information on the mechanisms of corrosion and possible new corrosion testing techniques. Corrosion potential, DC resistance, AC impedance at room temperature, AC impedance as a function of temperature, current flowing through coating at high potential, repetitive cathodic polarization, cathodic delamination, and current/time measurements can also provide valuable information related to corrosion rate and performance. (Leidheiser, 1991).

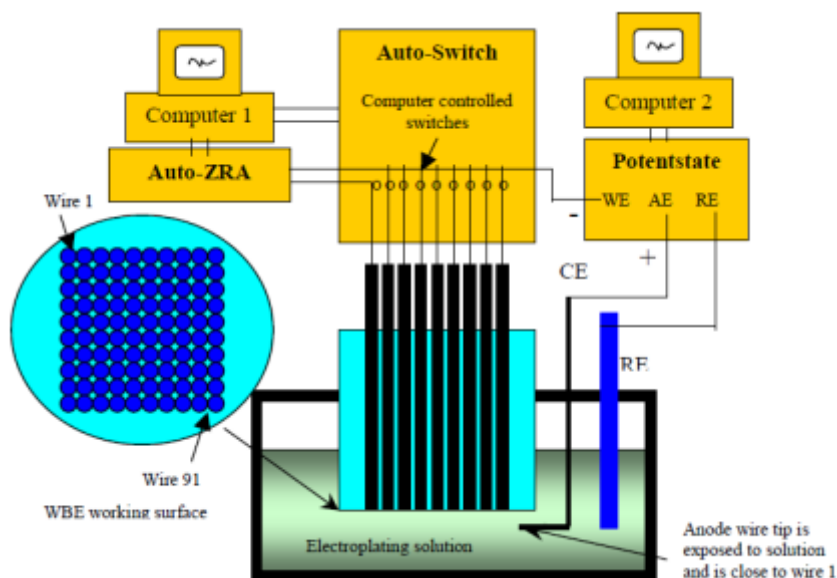


Figure 8. Electroplating and electro-dissolution experimental setup.

2. Online Monitoring Systems

On-board/online monitoring systems are being developed to provide valuable real time corrosion information effectively reducing corrosion maintenance costs, offering alternative corrosion maintenance approaches, and improving safety standards. The typical schedule based approach can be replaced with a condition based approach. These systems are able to provide early detection and assessment of corrosion. Monitoring systems also can be used to estimate service life and assess performance of corrosion inhibitors.

Since corrosion under a coating is difficult to detect, a reliable monitoring system would provide real-time evaluation of coating performance. For example, Dr. Sun, a professor from Ohio State University, used coupled multielectrode corrosion sensors and a multielectrode corrosion analyzer as an online monitoring system to study the corrosion under coatings. Different commercial coatings were applied to the electrodes and some electrodes were scratched to simulate defects. The electrodes were exposed to a salt solution. It has been concluded that the coupled multielectrode system is effective as an online corrosion monitoring system for coating performance. The high sensitivity of the sensors enabled obtaining early warnings before failure of the coatings were observed (Sun, 2005).

Sensor networks used under coatings can also decrease the costs of replacement and inspection if implemented early during the design stage. Many advantages are offered through sensor networks including continuous monitoring.

A significant advantage of impedance sensors is that it directly detects degradation and can detect moisture absorbed by a coating (Davis et al., 2000). Impedance based sensor technology was presented as a monitoring system to track the degradation of a coating system. The use of a single

high frequency perturbation provided fast collection of large volumes of data for analysis. Bayesian techniques were used to process the data and provide more accurate results while reducing errors caused by noise and sensor failures. Limitations with this technique occurred when corrosion was present but impedance values remained high which was caused by coating failure at an edge, therefore a clear understanding of the system is critical in the evaluation of the data (**Dante et al., 2007**). It has been shown that the sensitivity of the sensor varies with the frequency at which the data is collected. Mote based sensor technologies offered on-board monitoring and wireless data transmission (**Jakab et al., 2008**).

An analysis of a bimetallic corrosion sensor developed by NAVAIR, which involves a simple bimetallic sensor of different metal thin films, suggested advantages with its simple design and user-friendly real time data system (**Garosshen and Mukherji, 2000**).

A system with transducer interface modules and network capable application processors that monitors, records, and analyzes data from environmental and corrosivity sensors is examined for application in aircraft corrosion monitoring. The system is capable of not only measuring and evaluating the corrosiveness of the environment but also the corrosion of the structure. The sensors are equipped for measuring environmental factors such as temperature, relative humidity, time of wetness and electrochemical potential, which provides useful corrosion information. Furthermore, corrosion monitoring sensors capable of directly measuring the instantaneous rates and overall result of corrosion are utilized. This is accomplished by obtaining linear polarization resistance measurements and integrating over time to provide the total corrosion of the material (**Demo et al., 2009**).

Table 2. Corrosion sensor technology for aircraft applications. (Garosshen and Mukherji, 2000)

Sensor Type	Principle of Operation	Ref.
Bimetallic Thin Film Galvanic Sensor	Galvanic corrosion current between two dissimilar metals is measured by a ZRA.	3
Electrical Resistance (ER) Probes	Resistance change of metallic thin films are measured via ohmmeter data logger.	4
Linear Polarization Resistance (LPR)	Micro reference, working & counter electrodes to measure linear polarization resistance.	5
Bragg Grating Fiber-Optic Corrosion Sensor	Stress change in optical fiber occurs when metal coating corrodes. This changes fiber's refractive index and causes optical signal modulation.	6
LPR/ER Corrosion Sensor	Combines LPR and ER techniques into one sensor package to enable cross-referencing.	7
Micro Corrosion Sensor Array	Combines micropotentiostat and ZRA on a small chip to measure corrosion rate of real metallic sample versus environment.	8
Micro Ion-Selective Corrosion Sensor	Utilizes micro pH, chloride, and free potential electrodes to measure corrosion rate of aluminum sample.	9
Fiber Optic Fluorescence Corrosion Sensor	Detects light that is emitted from fiber coating that undergoes fluorescence in presence of corrosion products.	10

Fluorescence Paints	Paints containing additives that exhibit fluorescence under UV light in presence of corrosion products such as A1 +3.	11
Test Coupons	Metal coupons in aircraft are periodically examined for extent of corrosion visually and via weight loss measurements.	12

While sensor technology is improving, Ayello et al. studied three different techniques for the detection of corrosion. These systems, direct impedance measurements, galvanic couple with active RFID tags, and Wi-Fi based motes with 2 wire electrodes, were analyzed for the use of detecting corrosion under insulation. Impedance measurement indirectly predicts corrosion under insulation through time of wetness data. The Wi-Fi based sensors were determined to have many advantages over other detection techniques. These sensors continuously collect data and store information for remote access and are easily installed (**Ayello et al., 2011**).

Wire beam electrodes can also be used to collect data from various environments to estimate the pitting sensitivity of metals. The results demonstrated that materials, solutions, and exposure time affect the potential range of the wire beam electrode. It was exhibited that as the NaCl concentration increased logarithmically, the potential ranges of the wire beam electrode increased linearly. It was also determined that in NaCl solutions carbon steels had less pitting sensitivity than stainless steels although carbon steels were generally more susceptible to corrosion. Data collected included potentials, galvanic currents, and impedance. This technique of using wire beam electrodes to assess pitting corrosion was concluded to be better and more accurate than tradition methods (**Weng, 2004**).

Online corrosion monitoring technologies have played important roles in decreasing corrosion damage and failures, while increasing accuracy of data. Field corrosion monitoring consists of either a technique in which collective damage measurements are obtained or measurements of dominant corrosion rates are taken. The accumulated loss techniques indicate change only when an adequate amount of corrosion has occurred to change the bulk material properties, therefore, these systems are not used with online monitoring methods. However advances in multi-technique systems increase accuracy by providing multiple measurements within the system. These quantitative corrosion measurements can be delivered using the same communication methods and provide critical data for process control and optimization. By assessing the corrosion current, the direct result of the instantaneous corrosion process, the rate of metal loss can be determined (**Kane et al., 2005**).

3. Conclusions

Significant impacts can be observed when using test methods and online monitoring systems for corrosion protection. These methods will ultimately lead to great improvements in corrosion protection. Online corrosion monitoring provides valuable real time corrosion information, which can effectively reduce corrosion maintenance costs, offer alternative corrosion maintenance approaches, and improve safety standards. These systems are able to provide early detection and assessment of corrosion, and also can be used to estimate service life and assess performance of corrosion inhibitors. Although many test methods and online corrosion monitoring systems have been developed, the corrosion process is complicated and it is still necessary to explore new theories, methods and technologies to address the existing problems and bridge knowledge gaps.


References


- Ault, P. J. "Corrosion Durability Testing of Military Vehicles." *Metal Finishing*, 1999.
- Ayello, F., Hill, D., Marion, S., Sridhar, N. "Integrated Sensor Networks for Corrosion Under Insulation: Monitoring, Cost Reduction, and Life Extension Strategies." *Corrosion*, 2011.
- Bierwagen, G. P., He, L., Li, J., Ellingson, L., Tallman, D. E. "Studies of a New Accelerated Evaluation Method for Coating Corrosion Resistance- Thermal Cycling Testing." *Progress in Organic Coatings*, 2000, 39, 67-78.
- Chappelow, C.C., McElroy, A.D., Blackburn, R.R., Darwin, D., de Noyelles, F.G., Locke, C.E. "Handbook of Test Methods for Evaluating Chemical Deicers." Strategic Highway Research Program Report No. 332 (SHRP H-205.7) National Research Council, 1992.
- Collazo, A., Novoa, X.R. , Perez, C. , Puga, B. "The corrosion protection mechanism of rust converters: An electrochemical impedance spectroscopy study." *Electrochimica Acta*, 2010, 55, 6156-6162.
- Dante, J., Price, K., Sabata, A., Sabata, B. "Embedded Coating Degradation Sensors for Monitoring Performance of Temporary Coatings." *Corrosion*, 2007.
- Davis, G. D., Dacres, C. M., Krebs, L. A. "EIS-Based In-Situ Sensor for the Early Detection of Coatings Degradation and Substrate Corrosion." *Corrosion*, 2000.
- Demo, J., Steiner, A., Friedersdorf, F., Putic, M. "Development of a Wireless Miniaturized Smart Sensor Network for Aircraft Corrosion Monitoring." *IEEEAC*, 2009.
- Garosshen, T. J., Muhkherji, T. K. "On the Correlation of Bimetallic Corrosion Sensor Output to Actual Corrosion Damage." *Corrosion*, 2003.
- Granata, R. D. "Nonmetallic Coatings." *Corrosion Tests and Standards: Application and Interpretation-Second Edition*, 2005, 632-636.
- Jakab, M. A., Tormoen, G. W., Dante, J. F. "Measurement of CPC Performance Using EIS Based Sensor Methods- Laboratory and Field Studies." *Corrosion*, 2008.
- Kane, R. D., Eden, D. C., Eden, D. A. "Real-Time Solutions Integrate Corrosion Monitoring with Process Control." *Materials Performance*, 2005, 36-41.
- Kinzie, R. C. "Measuring the Rates and Impact of Corrosion Damage." *Aircraft Engineering and aerospace Technology*, 2003, 75 (2), 123-129.
- Leidheiser Jr., H. "Electrochemical Methods for Appraising Corrosion Protective Coatings." *The Journal of Coatings Technology*, 1991, 63, (802).
- Pacific Northwest Snowfighters, 2004. "Snow and Ice Control Chemical Products Specifications and Test Protocols for the PNS Association of British Colombia, Idaho, Montana, Oregon, and Washington."
- SAE J2334, 1998. "Cosmetic Corrosion Lab Test." SAE International, Warrendale, PA, June, 1998.

- Schmidt, D.P., Shaw, B.A. Sikora, E., Shaw, W.W., Laliberte, L.H. "Corrosion protection assessment of sacrificial coating systems as a function of exposure time in a marine environment." *Progress in Organic Coatings*, 2006, 57, 352-364.
- Schmidt, D.P., Shaw, B.A. Sikora, E., Shaw, W.W., Laliberte, L.H. "Comparison of Testing Techniques Used to Analyze the Corrosion Resistance of Sacrificial Coating Systems." *Tri-Service Corrosion Conference*, 2005, 1-29.
- Sharman, S. "Evaluation and Performance of Chemical Surface Treatments for Maintenance." *Corrosion* 2009, 1-17.
- Shi, X., Fay, L., Yang, Z., Nguyen, T.A., Liu, Y. "Corrosion of Deicers to Metals in Transportation Infrastructure: Introduction and Recent Developments." *Corrosion Reviews*, 2009, 27, 23-52.
- Sun, X., "Online Monitoring of Undercoating Corrosion Using Coupled Multielectrode Sensors." *Materials Performance*, 2005, 28-32.
- Tan, Y.-J. "Wire Beam Electrode: A New Tool for Studying Localized Corrosion and Other Heterogeneous Electrochemical Processes." *Corrosion Science*, 1999, 41, 229-247.
- Tan, Y.-J., Bailey, S., Kinsella, B. "Mapping Non-Uniform Corrosion Using the Wire Beam Electrode Method. II. Crevice Corrosion and Crevice Corrosion Exemption." *Corrosion Science*, 2001, 43, 1919-1929.
- Tans, Y.-J., "Measuring Electrochemical Noise Resistance from a Wire Beam Electrode Surface for Corrosion Rate and Pattern Determination." *Fluctuation and Noise Letters*, 2003, 3 (4), L419-L432.
- Wang, Y., Underhill, R.S., and Klassen, B. "Review of Corrosion Control Programs and Research Activities For Army Vehicles." *Defense R&D Canada- Atlantic. Technical Memorandum. DRDC Atlantic TM 2006-055*. 2006. <http://pubs.drdc.gc.ca/PDFS/unc53/p526285.pdf> accessed July 2008.
- Weng, Y. "New Sensors of Wire Beam Electrodes (WBE) to Detect Pitting Sensitivity of Steels." *Corrosion*, 2004.
- Yang, L., Sridhar, N., Brossia, C. S., Dunn, D. S. "Evaluation of the Coupled Multielectrode Array Sensor as a Real-Time Corrosion Monitor." *Corrosion Science*, 2005, 47, 1794-1809.

Appendix B: Survey of the Current Practices

On the basis of the literature review, the research team designed and distributed one online survey to document the current practice related to best practices or products used by various industries and agencies to protect their vehicles or equipment from the corrosive effects of chloride deicers. The survey was published online at: <https://www.surveymonkey.com/s/ZL77RPB> and distributed to various professional forums, groups (including NACE Corrosion Network, Corrosion Forum, Corrosion Discussion Forum, Corrosion Engineering Forum, Materials Forum, Concrete Forum, and other targeted experts). The following sections present the main results from the survey.

1. Name:	 Download	
	Response	Count
	Show Responses	105
	answered question	105
	skipped question	2

2. Title:	 Download	
	Response	Count
	Show Responses	105
	answered question	105
	skipped question	2

3. Organization/Agency:	Download
	Response Count
Show Responses	105
answered question	105
skipped question	2

4. Phone # and/or e-mail address:	Download
	Response Count
Show Responses	105
answered question	105
skipped question	2

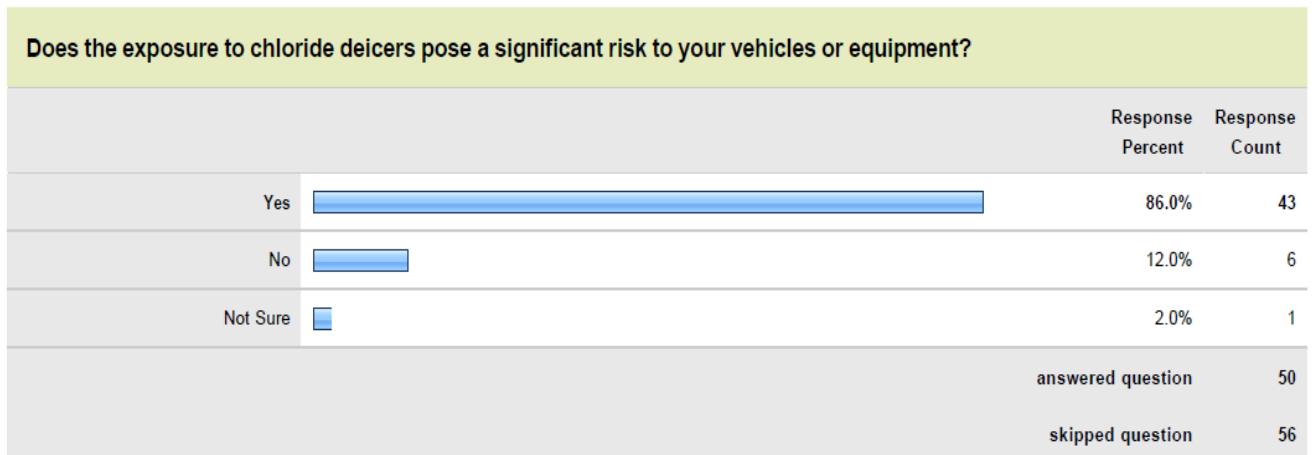
Some companies/agencies from which responses were obtained (with the specific response date in each bracket):

Mott MacDonald (6/26/2012), Town of Lexington, MA (5/9/2012), Virginia Department of Transportation (5/1/2012), Michigan Department Of Transportation (4/26/2012), CAN-AM INFRASTRUCTURE GROUP (4/24/2012), Kansas Department of Transportation (4/23/2012), The Hittle Snow Company, Inc. (4/23/2012), Kentucky Transportation Cabinet/Division of Maintenance (4/20/2012), Great Lakes Chloride, Inc. (4/18/2012), California Dept. of Transportation (4/18/2012), Ontario Ministry of Transportation (4/18/2012), Purdue University / Indiana LTAP (4/18/2012), City of Fargo, ND (4/18/2012), Quality First Consultants LLC (4/17/2012), Liquid Corrosion Control Inc. (4/17/2012), Alabama Dept. of Transportation (4/17/2012), City of Barrie (Ontario, Canada) (4/17/2012), Idaho Transportation Department (4/11/2012), South Dakota Dept. of Transportation (4/10/2012), Nevada Dept. of Transportation (4/9/2012), Pennsylvania Department of Transportation (4/9/2012), Tennessee Department of Transportation (4/9/2012), Krown (4/7/2012), Oregon Dept. of Transportation - Office of Maintenance & Operations (4/6/2012), NDOT District II (4/6/2012), Abibzankazzy Technical Limited (4/5/2012), RIDOT Division of Highway & Bridge Maintenance (3/28/2012), New York State Department of Transportation (3/23/2012), Arizona Department of Transportation (3/19/2012), Illinois Department of Transportation (3/19/2012), City of Farmington Hills, MI

DPW (3/16/2012), ST.Croix County Hwy. Dept. (3/15/2012), Vermont Agency of Transportation (DOT) (3/7/2012), Michigan Dept. of Transportation (3/7/2012), MRDC Operations Corporation (3/6/2012), WSDOT (2/28/2012)

1. Survey of the Best Practices to Protect Vehicles/Equipment from Chloride Deicers

Best Practices to Protect Vehicles/Equipment from Chloride Deicers



6. Please rank the risk of metallic corrosion to the types of equipment your agency owns.								Create Chart	Download
	Not Applicable	Very Low	Low	Moderate	High	Very High	Rating Average	Response Count	
Dump trucks	6.4% (3)	4.3% (2)	4.3% (2)	14.9% (7)	21.3% (10)	48.9% (23)	4.87	47	
Liquid deicer applicators	2.3% (1)	4.5% (2)	13.6% (6)	25.0% (11)	20.5% (9)	34.1% (15)	4.59	44	
Hoppers	7.0% (3)	7.0% (3)	9.3% (4)	27.9% (12)	23.3% (10)	25.6% (11)	4.30	43	
Front end loaders	4.5% (2)	4.5% (2)	15.9% (7)	25.0% (11)	25.0% (11)	25.0% (11)	4.36	44	
Supervisor trucks or crew pickups	2.2% (1)	6.5% (3)	26.1% (12)	37.0% (17)	21.7% (10)	6.5% (3)	3.89	46	
Graders	17.8% (8)	15.6% (7)	24.4% (11)	28.9% (13)	8.9% (4)	4.4% (2)	3.09	45	
Other (please specify)								10	
Hide Responses									

5/1/2012: Various other trucks and equipment used when deicing chemicals are deployed.

4/18/2012: Hand Tool and Shop equipment/support beams in equipment barns/snowplows


4/18/2012: Ships

3/16/2012: Trailers

3/13/2012: Facilities that store the equipment and areas the equipment is cleaned

3/7/2012: although salt spreaders and brine spreaders do not suffer much, the trucks on which they are mounted experience a lot of corrosion

3/6/2012: Tow plows, safety warning trucks, message boards, tankers, low boys, tractors (semi), blowers, signal trucks, sweepers, catch basin cleaners, haul trailers, fire trucks, wreckers

7. How many vehicles or equipment does your agency own that are at the risk of metallic corrosion? What is the estimated value of such assets (in US dollars)?		 Download
	Response	
	Count	
	Hide Responses	47

5/9/2012: 45, \$4.5MIL

5/1/2012: 7500 units. \$395,398,407.33 depreciated value.

4/26/2012: 150 combined vehicles and equipment (30,000,000)

4/25/2012: 50 trucks, 8 loaders of varying size. Value 500-600,000

4/22/2012: 8 trucks. Approximately \$800,000

4/22/2012: \$200,000 each

4/19/2012: 20 Vehicles. \$2.5 million

4/18/2012: At Indiana LTAP we serve cities town & counties most have a high number of equipment in their fleet and in their community

4/9/2012: 70 dump trucks/with sander units (70 x 250,000) = \$17,500,000. 25 loaders (25 x 200,000) = \$5,000,000 5 anti-icing units (5 x 15,000) = \$75,000

8. Does your agency track the direct cost of deicer-induced corrosion? Please comment as well. Download	
	Response Count
Hide Responses	47

3/28/2012: 515 pieces of equipment, estimated value \$50 million

4/25/2012: No, but does this refer to extra exposure units' actually spreading anti/deicers face, or the entire fleet which operates on chloride treated roads







4/17/2012: At this time we do not track agency deicer induced corrosion because here in Alabama we have a limited amount of snow and ice.

4/11/2012: Not at this time, but we are making modifications to our processes to capture these costs.

4/6/2012: Yes, estimated at \$535,000 annual loss of life

3/13/2012: Not nearly as close as we should. We have just recently become proactive in our approach to corrosion. We have begun the arduous process of evaluating the cost effectiveness of several corrosion reduction products.

3/7/2012: Not really, we estimate 300 euro per salt-spreading vehicle per year for anti-corrosion treatment

9. Please estimate your agency's annual expenditure on managing the corrosion of vehicles/equipment caused or aggravated by exposure to chloride deicers (in US dollars).			Download
		Response Percent	Response Count
Training programs Show Responses		89.8%	44
Materials selection [high-quality primers & topcoats, weather-proof terminations e.g., buss-style connectors and compression fittings, use of dielectric products, etc.] Show Responses		85.7%	42
Design improvements [e.g., eliminating junction boxes wherever possible] Show Responses		81.6%	40
Corrosion monitoring/testing Show Responses		75.5%	37
Preventative maintenance [protecting components prior to installation, regular washing/rinsing with or without corrosion inhibitors, after-market rust-proofing e.g., coatings, etc.] Show Responses		81.6%	40
Reactive maintenance [neutralizing existing corrosion via abrasive blasting/steam cleaning/chloride neutralizer spray; localized cleaning of the area and material that show signs of corrosion; etc.] Show Responses		83.7%	41
answered question			49
skipped question			58

Some company/agency responses from each question:

Training programs:

5/9/2012: \$500

4/26/2012: \$300,000

4/22/2012: \$200

4/6/2012: \$10,000

4/5/2012: effects of corrosion are incorporated in standard training electrical

3/28/2012: \$5000-\$10000

3/28/2012: \$150,000 estimated

3/23/2012: \$10,000

3/19/2012: \$40,000

3/16/2012: Pre-Winter and Post Storm Wrap Ups...5K Est.

3/7/2012: \$5000

Materials selection [high-quality primers & topcoats, weather-proof terminations e.g., buss-style connectors and compression fittings, use of dielectric products, etc.]:

5/9/2012: \$5,000

4/18/2012: \$20000

4/11/2012: \$100,000

4/9/2012: \$100,000.00 annually

4/6/2012: \$50,000

3/28/2012: \$50,000 estimated

3/13/2012: \$5000.00

3/7/2012: \$2,000,000

3/7/2012: \$10,000

3/7/2012: 100k to 200k

Design improvements [e.g., eliminating junction boxes wherever possible]:

4/9/2012: \$5,000.00 bi-annually

4/6/2012: \$10,000

3/28/2012: 15,000 estimated

3/23/201: \$50,000

3/7/2012: 25k - 100k

3/7/2012: \$10,000.00

3/6/2012: \$5,000

Corrosion monitoring/testing:

4/6/2012: \$1,000

3/23/2012: \$10,000

3/7/2012: \$1000.00

3/6/2012: \$2,000

Preventative maintenance [protecting components prior to installation, regular washing/rinsing with or without corrosion inhibitors, after-market rust-proofing e.g., coatings, etc.]:

5/9/2012: \$3,000

4/26/2012: \$500,000

4/25/2012: 3000 min, we do wash every vehicle used on treated roads after each event

4/18/2012: \$25000

4/11/2012: \$1M

4/9/2012: \$45,546.00 annually

4/6/2012: \$50,000

3/28/2012: \$25000

3/16/2012: Power Wash-PM equipment after an event...100K Est.

3/13/2012: \$10000.00

3/12/2012: \$4,500.00

3/7/2012: 100k to 200k

3/7/2012: \$8,000.00

Reactive maintenance [neutralizing existing corrosion via abrasive blasting/steam cleaning/chloride neutralizer spray; localized cleaning of the area and material that show signs of corrosion; etc.]:

5/9/2012: \$2,000

4/26/2012: \$300,000

4/25/2012: 5000 salt app units have bodies and to the extent possible undercarriages painted each season

4/9/2012: \$200,000.00 annually

4/6/2012: \$200,000

3/28/2012: \$25,000 estimated

3/23/2012: \$600,000







3/13/2012: \$15000.00

3/7/2012: 30k - 50k

3/6/2012: \$25,000

10. Please estimate other costs of deicer corrosion to your agency's vehicles/equipment (in US dollars and/or in %).

[Download](#)

		Response Percent	Response Count
Vehicles/equipment depreciation in value Show Responses		93.9%	46
Vehicles/equipment downtime Show Responses		79.6%	39
Reduction in vehicles/equipment's reliability Show Responses		75.5%	37
Reduction in vehicles/equipment's service life Show Responses		79.6%	39
Premature repair or replacement of corroded parts, including both materials and labor Show Responses		77.6%	38
Safety of operators and others due to faulty components; etc. Show Responses		67.3%	33
		answered question	49
		skipped question	58

Some company/agency responses from each question:

Vehicles/equipment depreciation in value:

4/26/2012: 10% per year

4/25/2012: 3-5% each season in use as a service vehicle

4/18/2012: 6% yearly

4/17/2012: Very little due to corrosion

4/11/2012: 20% if corrosion was not present

4/9/2012: \$1,000,000 per year for total fleet

4/6/2012: \$535,000 annual loss of life costs

4/5/2012: Full treatment of a semi unit would be approx. \$450.00

3/23/2012: 40%

3/19/2012: 5%

3/12/2012: \$5-7,000.00

3/9/2012: \$1600.00 in soap and waxes

3/8/2012: 2%

3/7/2012: \$1M

3/7/2012: \$80,000,000

3/7/2012: 10% annually

3/6/2012: \$200,000.00

Vehicles/equipment downtime:

4/25/2012: an extra 10% due to electrical corrosion and rust issues primarily to brake, trans cooler and fuel lines

4/19/2012: 5%

4/18/2012: 15% yearly

4/9/2012: \$250,000 per year

4/5/2012: Eliminate 99% of electrical corrosion in plugs and appliances but also between double frames.

4/5/2012: snow districts down time about 20% higher than valley areas

3/23/2012: 50%

3/16/2012: 50% of down time is corrosion related

3/13/2012: \$15000.00

3/12/2012: \$5,000.00

3/9/2012: Average of 3 hours per week

3/7/2012: \$100K

3/7/2012: 10%

3/6/2012: 250,000.00

Reduction in vehicles/equipment's reliability:

4/25/2012: 10%, ties into repairs

4/19/2012: 10%

4/9/2012: 250,000 per year

4/5/2012: If treated when assembling between the double frames these frames would never rust between them.

3/23/2012: 40%

3/16/2012: Our trucks lose their reliability in an average of 6 years

3/6/2012: 500,000.00

Reduction in vehicles/equipment's service life:

5/9/2012: 20%

4/25/2012: 15% over an average fleet life of 7-9the years of duty as a salt app unit, less for plowing or shovel crew units

4/22/2012: 10%

4/9/2012: 5 to 10 year per unit

3/23/2012: 25%

3/16/2012: Life span is reduced by an average of 5 years

3/12/2012: \$4,500.00

3/9/2012: 55%

3/7/2012: 20%

3/7/2012: 50% per vehicle

3/6/2012: \$750,000

Premature repair or replacement of corroded parts, including both materials and labor:

5/9/2012: 20%

4/25/2012: 15-25% less service life

4/19/2012: 20%

4/9/2012: 150,000 per year

4/9/2012: \$150,000.00 annually

4/5/2012: Varies year to year approx. \$50,000 in fuel tanks stand out this year

3/23/2012: 50%

3/12/2012: \$5,000.00

3/12/2012: Yes, 3-4 years start to replace electrical

3/9/2012: 45%

3/7/2012: \$90,000

3/7/2012: \$100K

3/7/2012: 20k-50k

3/6/2012: \$50,000

Safety of operators and others due to faulty components; etc.:

4/25/2012: We have fortunate that no accident involving a serious loss or injury have occurred, most often potential problem areas in this regard such a corroded brake line have been found in post/pre trip mechanical inspections or when in the shop for pm services

4/19/2012: 10%

3/28/2012: Less than 1%

3/23/2012: 5%

3/7/2012: \$30,000

11. Please rank the type of deicers your agency's vehicles/equipment are mostly exposed to.

[Create Chart](#) [Download](#)

	Not Applicable	Very Rare	Rare	Moderate	Frequent	Very Frequent	Rating Average	Response Count
Salt	2.6% (1)	2.6% (1)	5.3% (2)	10.5% (4)	13.2% (5)	65.8% (25)	5.26	38
Corrosion Inhibited Salt	37.1% (13)	11.4% (4)	20.0% (7)	11.4% (4)	2.9% (1)	17.1% (6)	2.83	35
Pre-wetted salt	10.0% (4)	2.5% (1)	5.0% (2)	2.5% (1)	30.0% (12)	50.0% (20)	4.90	40
Sand/Salt Blend	14.3% (5)	11.4% (4)	5.7% (2)	17.1% (6)	17.1% (6)	34.3% (12)	4.14	35
Magnesium Chloride	28.9% (11)	15.8% (6)	10.5% (4)	21.1% (8)	13.2% (5)	10.5% (4)	3.05	38
Corrosion Inhibited Magnesium Chloride	32.4% (12)	18.9% (7)	16.2% (6)	5.4% (2)	8.1% (3)	18.9% (7)	2.95	37
Calcium Chloride	22.5% (9)	12.5% (5)	20.0% (8)	25.0% (10)	10.0% (4)	10.0% (4)	3.18	40
Corrosion Inhibited Calcium Chloride	50.0% (17)	14.7% (5)	2.9% (1)	11.8% (4)	11.8% (4)	8.8% (3)	2.47	34
Sodium Chloride Brine	18.4% (7)	2.6% (1)	7.9% (3)	10.5% (4)	21.1% (8)	39.5% (15)	4.32	38
Corrosion Inhibited Sodium Chloride Brine	48.6% (17)	17.1% (6)	11.4% (4)	11.4% (4)	0.0% (0)	11.4% (4)	2.31	35
Non-Chloride Deicers	53.1% (17)	25.0% (8)	3.1% (1)	6.3% (2)	6.3% (2)	6.3% (2)	2.06	32
Other (please specify) Hide Responses								5

4/22/2012: Cold temperature modified mag chloride with corrosion inhibitor mixed with sand.

3/16/2012: We mix Beet Juice in with our sodium chloride

3/13/2012: Sugar based products

3/7/2012: Prussian blue

12. What are the approximate tonnages of deicers exposed by your agency's vehicles/equipment on an annual basis? What are typical application rates for solid and liquid deicers? [Download](#)

	Response Count
Hide Responses	35

5/9/2012: 5,000 tons

5/1/2012: 443,000 tons of salt per year, 684,000 gallons of liquid calcium chloride per year, 112,000 gallons of liquid magnesium chloride per year, 330 pound of salt per lane mile. Base on Salt Institute guidelines. 30 gallons of salt brine per lane-mile based on Salt Institute guidelines.

4/26/2012: 50,000 ton 450 max application rate

4/23/2012: 80,000 ton of salt. 2,000,000 gallon salt brine

4/19/2012: 200 tons. 300lbs.per lane mile&30 gallons liquid per ton of salt





4/12/2012: Solid Salt - 200 lbs./Lane Mile, Liquid NaCl - 30 gal/lane mile, Liquid MgCl₂ - 30 gal/lane mile.

4/9/2012: 20,000 ton of salt 500 tons of Mag Chloride liquid anti-icers.

3/13/2012: 6000 tons of solid deicers.5000 tons of pre-wet abrasives. All products are pre-wet at the time of application. Based on conditions and liquid blends, we average 26 gallons per ton of salt and 10 gallons per ton of abrasive. The typical application rate is 350 lb. per

13. What type of climatic environment do your agency's vehicles/equipment operate in?

[Create Chart](#) [Download](#)

		Response Percent	Response Count
Dry & Cold		12.1%	4
Wet & Cold		69.7%	23
Dry & Mild Cold		3.0%	1
Wet & Mild Cold		15.2%	5
Other (please specify)			10
		Hide Responses	

lane mile.

5/1/2012: All of the above depending upon current weather.

4/9/2012: we operate in all of them dry and cold is the most common.

4/6/2012: All types, Oregon has a very diverse climate

4/5/2012: All conditions

3/7/2012: Although our contracts are primarily in dry& cold areas, we also have vehicles in

14. Please rank the risk of chloride deicers to various components of your agency's vehicles/equipment.							
	Not Sure/Not Applicable	Very Low	Relatively Low	Moderate	Relatively High	Very High	Response Count
Brackets and supports	5.0% (2)	0.0% (0)	2.5% (1)	27.5% (11)	32.5% (13)	32.5% (13)	40
Brake drums and disks	2.5% (1)	5.0% (2)	7.5% (3)	20.0% (8)	35.0% (14)	30.0% (12)	40
Brake air cans	2.5% (1)	2.5% (1)	7.5% (3)	20.0% (8)	32.5% (13)	35.0% (14)	40
Brake lines	5.0% (2)	7.5% (3)	15.0% (6)	17.5% (7)	30.0% (12)	25.0% (10)	40
Bumpers	5.0% (2)	5.0% (2)	17.5% (7)	37.5% (15)	22.5% (9)	12.5% (5)	40
Body panels	0.0% (0)	2.5% (1)	7.5% (3)	37.5% (15)	35.0% (14)	17.5% (7)	40
Electrical wiring	0.0% (0)	0.0% (0)	0.0% (0)	7.5% (3)	40.0% (16)	52.5% (21)	40
Engines and drive train components	0.0% (0)	2.5% (1)	10.0% (4)	47.5% (19)	22.5% (9)	17.5% (7)	40
Exhaust systems/Mufflers	2.5% (1)	2.5% (1)	2.5% (1)	42.5% (17)	32.5% (13)	17.5% (7)	40
Fittings	2.5% (1)	0.0% (0)	5.0% (2)	27.5% (11)	35.0% (14)	30.0% (12)	40
Frames	2.5% (1)	2.5% (1)	0.0% (0)	20.0% (8)	47.5% (19)	27.5% (11)	40
Fuel tanks	0.0% (0)	0.0% (0)	12.5% (5)	35.0% (14)	35.0% (14)	17.5% (7)	40

all other three conditions

Radiators	2.5% (1)	0.0% (0)	10.0% (4)	50.0% (20)	20.0% (8)	17.5% (7)	40
Transmission housings	2.5% (1)	5.0% (2)	22.5% (9)	30.0% (12)	25.0% (10)	15.0% (6)	40
Trim	5.1% (2)	5.1% (2)	23.1% (9)	41.0% (16)	15.4% (6)	10.3% (4)	39
Wheels	2.6% (1)	5.1% (2)	12.8% (5)	15.4% (6)	43.6% (17)	20.5% (8)	39
-----DIVIDING-LINE-----	27.3% (3)	0.0% (0)	18.2% (2)	27.3% (3)	9.1% (1)	18.2% (2)	11
Granular hopper	5.6% (2)	19.4% (7)	5.6% (2)	2.8% (1)	30.6% (11)	36.1% (13)	36
Spreader auger	2.7% (1)	8.1% (3)	16.2% (6)	10.8% (4)	24.3% (9)	37.8% (14)	37
Spreader chute	5.3% (2)	5.3% (2)	10.5% (4)	7.9% (3)	31.6% (12)	39.5% (15)	38
Spreader disc	7.9% (3)	18.4% (7)	15.8% (6)	10.5% (4)	21.1% (8)	26.3% (10)	38
Spray bar	7.9% (3)	15.8% (6)	15.8% (6)	5.3% (2)	31.6% (12)	23.7% (9)	38
Liquid storage tanks	5.3% (2)	28.9% (11)	18.4% (7)	13.2% (5)	13.2% (5)	21.1% (8)	38
Plow blades/cutting edges	5.3% (2)	13.2% (5)	23.7% (9)	15.8% (6)	23.7% (9)	18.4% (7)	38
Hydraulic systems/pumps/hoses /cylinders/valves	2.6% (1)	5.3% (2)	7.9% (3)	21.1% (8)	36.8% (14)	26.3% (10)	38
Other (please specify) Hide Responses							6

4/12/2012: All chemical spreaders are either constructed of either poly or stainless steel.

4/5/2012: Wheels break due to tire chains don't have time to corrode, using plastic tanks

3/13/2012: Structural supports on body and chassis

3/6/2012: Oil Pans – High






15. Please select the common types of corrosion-prone material and their respective forms of corrosion seen in your agency's vehicles/equipment exposed to chloride deicers. Please send us some pictures if possible (xianming_s@coe.montana.edu). Thanks!

 [Create Chart](#)  [Download](#)

	General or uniform corrosion	Localized corrosion	Response Count
cast irons	81.3% (26)	21.9% (7)	32
aluminum alloys	55.9% (19)	50.0% (17)	34
magnesium alloys	68.2% (15)	36.4% (8)	22
copper and copper alloys	67.9% (19)	35.7% (10)	28
carbon steels	73.5% (25)	32.4% (11)	34
stainless steels	50.0% (12)	50.0% (12)	24
metallic coatings	64.0% (16)	40.0% (10)	25
metallic glass	56.3% (9)	43.8% (7)	16
composites	68.8% (11)	31.3% (5)	16
	Other (please specify) Hide Responses		3

4/25/2012: we use stainless salter units (vbox style) and have very few corrosion problems with the hoppers. Drag chains, bearings and other common steel components rust extremely quickly

16. Please estimate the cost and effectiveness of measures adopted by your agency that are effective in reducing the deicer corrosion to vehicles/equipment (in US dollars and/or in % extension of service life or in minimizing certain types of failure). Provide examples wherever possible. [Download](#)

		Response Percent	Response Count
materials selection practices Show Responses		89.2%	33
design improvements Show Responses		73.0%	27
corrosion monitoring/testing or training programs Show Responses		59.5%	22
preventative maintenance practices or products (wrapping of components prior to installation, regular washing, anti-corrosion coatings, corrosion inhibitors, etc.) Show Responses		75.7%	28
reactive maintenance practices or products (neutralizing existing corrosion, localized cleaning, rust converters, salt removers, etc.) Show Responses		70.3%	26
		answered question	37
		skipped question	70

Some company/agency responses from each question:

Materials selection practices:

4/12/2012: Effectively eliminates corrosion

4/9/2012: Use stainless steel in dump beds and sanders. Unknown value

4/9/2012: Material selection is NOT based on corrosion prevention, it is based on cost

4/6/2012: Selection doesn't factor equipment corrosion

4/5/2012: Stainless steel components last 25% to 100% longer

3/23/2012: \$5,000,000 60%

3/19/2012: 50% to 100%

3/16/2012: Stainless steel, custom made oil pans. \$900

3/16/2012: Not sure of figures, have seen a reduction in salt use with Pre-wet and Anti-icing practices.

3/13/2012: Unknown cost but and overall reduction in premature failure, Very effective

3/7/2012: This is difficult. We try to look at products that would be less corrosive and sealed very well for any/all products used in winter operations. I would not be able to estimate this cost.

Design improvement:

4/18/2012: purchasing stainless steel components - high cost

4/12/2012: 25% reduction in corrosion

4/5/2012: anywhere from resolution of problem to increasing the problem. Example metal to plastic light housings no more corrosion but brittle and brake in extreme cold

3/23/2012: \$2,000,000 35%

3/7/2012: This is difficult. We try to look at products that would be less corrosive and sealed very well for any/all products used in winter operations. I would not be able to estimate this cost.

Corrosion monitoring/testing or training programs:

4/19/2012: 5%

4/6/2012: Some monitoring and testing in house

3/19/2012: 10%

3/6/2012: Testing sacrificial anodes. \$0

Preventative maintenance practices or products:

4/19/2012: 90%

4/12/2012: 25% reduction in corrosion

4/9/2012: regular washing unknown value

4/6/2012: We have BMP's that are followed by some crews, others not so much.

4/5/2012: wrapping seems to hold corrosive materials in rather than protect

3/23/2012: \$100,000 35%

3/19/2012: 70%

3/16/2012: Grease all electrical connections, 1 hour per vehicle when new.

3/7/2012: 30%

3/7/2012: This is difficult. We try to look at products that would be less corrosive and sealed very well for any/all products used in winter operations. I would not be able to estimate this cost.

3/7/2012: 100% increase in truck life span: extremely cost effective

Reactive maintenance practices or products:

4/25/2012: 10%

4/19/2012: 50%

4/6/2012: Sand blast and repaint, powder coating and rust converters slow the process

4/5/2012: Including inside electrical plugs & computers

4/5/2012: Generally can't use because of storm water regulations

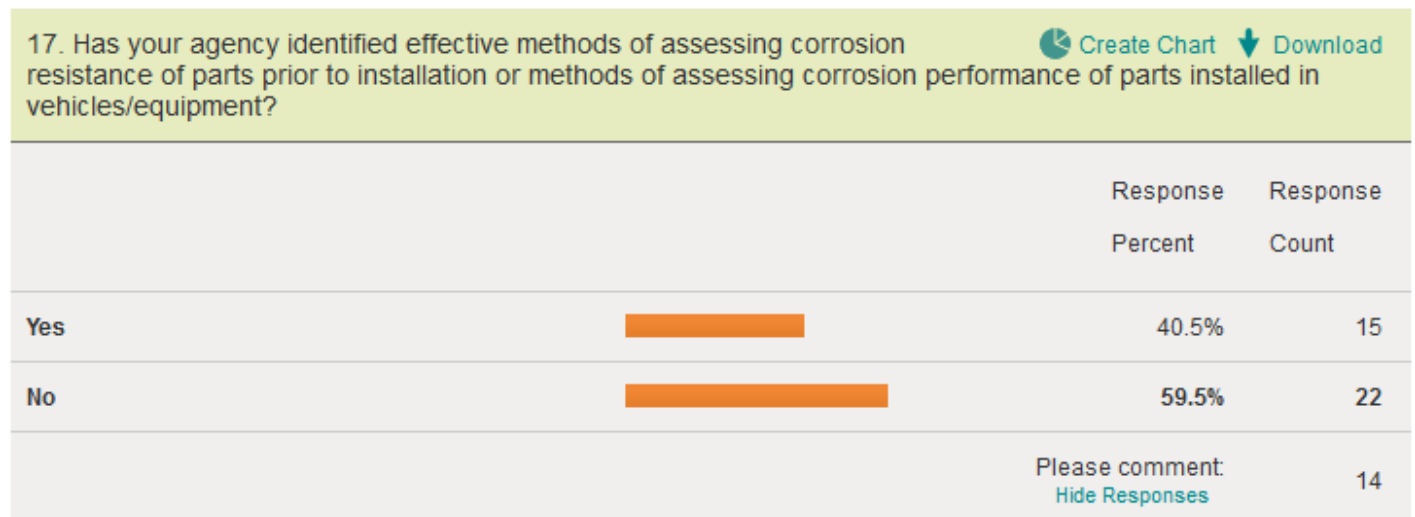
3/23/2012: \$10,000, 25%

3/16/2012: Hard to put a figure on washing of equipment. Just started using neutralizers

3/7/2012: 30%

3/7/2012: This is difficult. We try to look at products that would be less corrosive and sealed very well for any/all products used in winter operations. I would not be able to estimate this cost.

3/7/2012: 30% increase in truck life span: very cost effective



4/12/2012: Make as many components from stainless steel as possible

3/23/2012: We replace with stainless steel or poly wherever possible

3/19/2012: Mostly react to problems. Example Rhino lining on oil pans that fail.

3/13/2012: Through cleaning a regular application of vegetable oil seems to be the most cost effective answer for our operation.

3/12/2012: Preventive measures in maintenance or improvements work or they don't.

3/9/2012: The use of stainless Steel Couplers

3/7/2012: We rely on vendor salt spray testing.

3/6/2012: Various methods. Stainless steel is best

18. Please provide the brand name and vendor of several coatings, salt removers, corrosion inhibitors, or other products your agency have used in reducing deicer corrosion; and comment on their cost and effectiveness.		Download
		Response
		Count
Hide Responses		38

5/1/2012: Salt-Away. Lubre-seal

4/25/2012: We have used Rhomar wash and treatment but it is costly. Owners are short sighted on pm issue.

4/23/2012: Lubri-seal- for our spreader chains. We treat the spreader chains at least once a year.

4/22/2012: Rohmar industries for Neutro wash

4/18/2012: Component technologies wiring products AR400 - AR570 types of high carbon steels Stainless steels

4/9/2012: Good old soap and water as frequently and as soon as possible after a storm event.

4/7/2012: Krown T40 Krown KL73 Krown MR35 Salt Eliminator

4/6/2012: Zinc and powder coatings

3/13/2012: Metal Gard, VERY expensive and overall not effective, Ruatame (adscs) not effective Salt Neutralizer (share) effective cleaner, not an effective corrosion inhibitor RSDW Truck Gard, expensive and not effective LPS 2 & 3 (lps lab) VERY expensive and not very effective All the above

mentioned products are NOT environmentally friendly and have tough storage requirements We have had the best results with the use of a good panel wash and a coating of vegetable oil, this is also the only environmentally friendly product we have encountered that actually showed a noticeable result

3/12/2012: nutera wash from Romar Ind, Dawn dish soap pressure washer applied

3/7/2012: Stainless steel has been the number one change

3/7/2012: We are not currently utilizing any inhibitors. We have tested Salt Away (truck wash product) that appears to be somewhat effective if it is used on the entire truck, including underbody.

3/6/2012: Rhomar Salt Neutralizer - Very effective and cost effective GeoMelt - Moderate Costs - Moderate effectiveness

19. If applicable, please share with us some success stories or lessons learned and/or send us implementation recommendations, procurement specifications, maintenance guide, or other guidelines that reduce the corrosion of chloride deicers on vehicles/equipment. [Download](#)

Response

Count

[Hide Responses](#)

23

4/22/2012: Clean your equipment at the end of each storm.

4/19/2012: Wash vehicles and equipment as often as possible

4/18/2012: On board pre wetting tanks to spray bar not spinner disc / homemade device - Lake County Indiana

4/12/2012: stainless steel components and sealed lighting systems

4/6/2012: Playing with zinc anodes in the solution tanks grounded to frames.

4/5/2012: First coated Rusty older dodge snub nose 5 tones flat decks in 1987, which already had rust holes through the flooring. Welded in some patches, coated with Ship-2-Shore, now 25 years later the vehicle has been donated to the "Saanich Historical Artifacts Society" still looking as bad as it did 25 years ago.

4/5/2012: Electrical junction blocks mounted in cab when possible

3/23/2012: We retrofitted many trucks with stainless steel oil pans

3/19/2012: Use of stainless steel or corrosion resistant alloys for hoppers and spreaders. Junction boxes and protecting electrical wiring.

3/16/2012: We have been replacing the major trouble components with stainless steel parts, made in house or contracted out.

3/13/2012: We have incorporated several minor changes in our day to day operation in an effort to extend the service life of our equipment and reduce the down time associated with corrosion specific repairs. We have moved the liquid pre-wet nozzles to the spinner instead of the auger or chain. We have an active washing program and we are proactive in the application of vegetable oil. We have only recently begun to document the effectiveness of different encapsulation products and will be in a better position to comment in a few years. We have also found that prior to taking delivery of a chassis; we have all computer specific connections moved to the operators' compartment. We have also noticed better corrosion resistance to powder coat versus primer and paint.

3/9/2012: Calibration Training and proper washing techniques. Anticipate improvements resulting from implementing MDSS practices and protocols

3/7/2012: Stainless steel dump bodies, slide-in spreaders, and combination bodies' have increased the life of our winter maintenance trucks greatly

3/7/2012: We use stainless steel when at all possible and try to wash on a regular basis. We do not use an inhibitor at this time

3/7/2012: Our Company has been in winter maintenance for over 20 years, and our practices essentially come from "inherited wisdom". We have seen a steady increase in the serviceable life of vehicles due to preventive maintenance, especially regular washing of vehicles. Corrective maintenance is also extremely important, but regular washing and anti- corrosion coatings can double a vehicle's life span. We rarely have problems corrosion problems with spreaders, but we have a relatively modern fleet and purchase from reputed brands (mainly Schmidt), lately we have begun to We are currently planning a small study comparing different paints and inhibitors over a winter season. Be glad to hear your thoughts and share results

3/6/2012: Painted and powder coated components must be free from post coating work, (welds or drilled holes). Any interruption in the coating causes severe corrosion. Any surfaces that are bolted together on the frame or body allow MgCl₂ to wick into and get trapped there. These surfaces have severe corrosion showing after the bracket or plate is removed.

3/6/2012: Stainless steel on any metals is a tremendous asset. Thoroughly cleaning all equipment immediately after a storm and using a salt neutralizer is highly effective. Store equipment indoor after cleaning. Make sure you minimize any areas where salt or other deicer products cannot be cleaned.

2. KEY FINDINGS FROM THE SURVEY

2.1. Chloride Deicer Corrosion Problem

- Chloride deicers pose a significant risk to the vehicles or equipment, they cause a very high metallic corrosion to dump trucks, liquid deicer applicators and front end loaders; they cause a moderate metallic corrosion to hoppers, supervisor trucks or crew pickups and graders.
- The numbers of vehicles or equipment are at risk of metallic corrosion is colossal; the cost to maintain those equipment is also an overwhelmed number. Here are some values observed from the survey (annually): 515 pieces of equipment need \$50 million to maintain; 3,000 units need \$125 million to maintain; 80 units need \$11.6 million to maintain.

- Other expenses of deicer corrosion such as vehicles/equipment depreciation in value, vehicles/equipment downtime, reduction in vehicles reliability, safety of operators and others due to faulty components also showed a significant number. See Question 10 above.

2.2. Chloride Deicer Corrosion Causes

- There are four materials have been listed as “very frequently exposed” to vehicles in this survey. They are salt, pre-wetted salt, sand/salt blend and sodium chloride brine.
- Another discovery in this survey is that the tonnages of deicers exposed to the companies’ vehicles/equipment on an annual basis are more than expected. Here is one of the responses from the survey: 443,000 tons of salt per year. 684,000 gallons of liquid calcium chloride per year. 112,000 gallons of liquid magnesium chloride per year. 330 pound of salt per lane mile based on Salt Institute guidelines. 30 gallons of salt brine per lane-mile based on Salt Institute guidelines.
- The typical climatic environment where the surveyed agencies operated at are mostly in Wet & Cold climate.
- In the survey, several specific vehicles/equipment parts have been listed to verify the risk of chloride deicers caused to them. From the results we found that 32.5% of responses agree bracket and supports have a very high risk due to chloride deicers, 35% of responses agree brake drums and disks have a relatively high risk due to chloride deicers, and 52.5% of responses agree that electrical wiring have a high risk due to chloride deicers. Those data showed that the parts of vehicles and equipment are very vulnerable to corrosion that caused by chloride deicers.
- Besides the parts of vehicles/equipment, the types of corrosion-prone material in those agencies are also targeted for this survey. The corrosion that seen in those materials is also surprising. The cast irons used in those companies have an 81.3% of general or uniform corrosion, aluminum alloys have 55.9%, magnesium alloys have 68.2% and carbon steels have 73.5%, etc.

2.3. Best Practices or Products for Managing Chloride Deicer Corrosion

- The estimated cost for reducing the deicer corrosion to vehicles/equipment spend as much as “\$5 million with 60% of extended life (3/23/2012)” on material selection practices, “\$2 million with 35% of extended life (3/23/2012)” on design improvements. The corrosion monitoring/testing, preventative maintenance practices and reactive maintenance practices have spent less in reducing corrosion process.
- The efficient practices to prevent deicer corrosion have been identified as “Make as many components from stainless steel as possible”, “We replace with stainless steel or poly wherever possible”, and “The use of stainless Steel Couplers.” Those responses have showed that stainless steel is a most common way used for prevent chloride deicer corrosion.
- The best products that this survey identified for corrosion prevention are: Krown T40, Rust Bullet, Hold Tight, Salt Away, and Lebra-Seal. The category of those products is inhibitor, coating, and salt remover.
- Other success ways/recommendations for prevent corrosion is wash vehicles and equipment regularly, use zinc anodes in solution tanks, mount electrical junction blocks in cab, and power wash equipment after an even.